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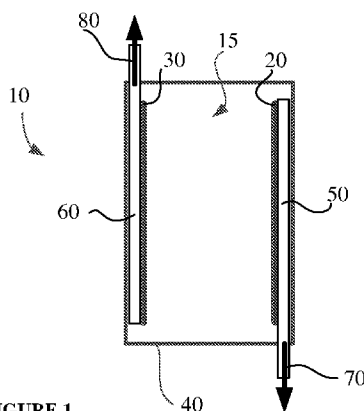


FIGURE 1

(57) Abstract: Disclosed are electrochemical cells and methods of use or operation, in which one or more gas-producing electrodes operate in a manner that is bubble-free or substantially bubble-free. Disclosed are electrochemical cells and methods of operation or use under conditions of intermittent and/or fluctuating currents. In one aspect there is provided a method for operating an electrochemical cell, and an electrochemical cell, wherein the electrochemical cell comprises: a gas-producing electrode; a counter electrode, the gas-producing electrode and the counter electrode being separated by an electrolyte. Preferably there is also provided one or more void volumes. The method comprises: supplying an intermittent and/or fluctuating current to at least the gas-producing electrode; and producing a gas at the gas-producing electrode as a result of an electrochemical reaction. Preferably the gas is received by the one or more void volumes.

ELECTROCHEMICAL CELL THAT OPERATES EFFICIENTLY WITH FLUCTUATING CURRENTS

TECHNICAL FIELD

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[001] The present invention relates to the efficient or improved operation of electrochemical cells that involve a gas-liquid interface, particularly, but not exclusively, to the efficient or improved operation of gas-liquid electrochemical cells under conditions of intermittent and/or fluctuating currents.

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BACKGROUND

[002] Numerous electrochemical cells facilitate liquid-to-gas or gas-to-liquid transformations that involve the formation of, or presence of gas bubbles in liquid electrolyte solutions. For example, electrochemical cells used in the chlor-alkali process typically generate chlorine gas and hydrogen gas in the form of bubbles at the anode and cathode, respectively.

[003] Bubbles in an electrochemical cell generally have the effect of increasing the electrical energy required to undertake the chemical transformation in the cell. This arises from effects that include the following:

- (1) Bubble formation: In order to create a bubble, supersaturated gas in the liquid electrolyte immediately adjacent to an electrode surface must combine to form a small bubble. The bubble is initially created by and held up by a large internal pressure (known as the ‘Laplace’ pressure). Such bubbles are typically very small and, since the Laplace pressure is inversely proportional to the internal pressure needed, they must necessarily contain high internal pressures of gas. For example, according to a thesis by Yannick De Strycker entitled “*A bubble curtain model applied in chlorate electrolysis*” (published by the Chalmers University of Technology, Goteborg, Sweden, in 2012), the hydrogen

- bubbles formed at the cathode in electrochemical chlorate manufacture at atmospheric pressure are estimated to initially be ca. 3.2 nm in diameter, so that their internal ('Laplace') pressures must be ca. 824 bar. The additional energy required to produce such bubbles is known in the art as the bubble overpotential. The bubble overpotential can be substantial. In the above-mentioned case, bubble formation by hydrogen at the cathode alone, was estimated to add ca. 0.1 V to the cell voltage. Once formed, the very small initial bubbles spontaneously expand as a result of their large internal pressure. In the above-mentioned case of hydrogen generation in chlorate manufacture at atmospheric pressure, the initial bubbles were found to expand to a diameter of ca. 0.1 mm, at which stage the pressure inside the bubble was equal to the pressure outside the bubble.
- (2) "Bubble coverage" / "Bubble curtain": Studies have shown that bubbles are typically formed in crevasses, clefts, or other micrometer- or nanometer-sized irregularities on electrode surfaces. This effect is driven by the fact that, according to the Laplace equation, the smaller the radius of a bubble, the higher the pressure inside the bubble must be to push the bubble up and to hold the bubble up. There is therefore a fundamental thermodynamic (energy) advantage to forming bubbles having small volumes but large radii. This can only occur within tiny crevasses, clefts or similar irregularities that may be present on many electrode surfaces. Bubbles formed within such features are not spherical but instead fill a portion – usually the deepest portion – of the feature. Such bubbles have very small volumes. However, the bubbles formed in such features have large radii that extend along the length of the cleft or irregularity. The larger radii mean that the internal pressure of such bubbles may be very much lower than a spherical bubble of the same volume. Such 'cleft'-based bubbles will therefore form at a lower level of electrolyte supersaturation with the gas in question, than will spherical bubbles. That is, the bubbles formed in such features, i.e.

‘cleft’-based bubbles, are favoured to form before spherical bubbles are formed on the electrode surface.

‘Cleft’-based bubbles of this type typically start within the ‘cleft’ feature on an electrode surface and then expand out of the cleft into a largely spherical shape. The resulting bubble is then held on the surface of the electrode by its attachment to the ‘cleft’ in which the bubble initially formed. The effect of having many such attached bubbles at the electrode surface is to create a bubble “curtain” between the liquid electrolyte and the active surface of the electrode. This “bubble curtain” (or “bubble coverage”) typically impedes movement of the electrolyte to the electrode surface, slowing or even halting the reaction. To overcome this effect, many electrochemical cells employ continuous mechanical pumping to sweep the electrolyte over the surface of the electrodes to dislodge surface bubbles. The resulting current drawn by the pump diminishes the overall electrical efficiency of the electrochemical cell.

- (3) Bubbles in conduction pathway (“Voidage”): Even after bubbles are released from an electrode surface into the electrolyte they still impede electrical efficiency in a cell. In electrical terms, a bubble is a non-conducting void within the conduction pathway that comprises of the liquid electrolyte between the two electrodes. The greater the number of, and relative volume of such non-conducting voids present, the greater the overall electrical resistance of the cell. This effect, which is known in the art as “voidage”, becomes particularly pronounced as the current density increases, when larger volumes of bubbles are produced. In the above-mentioned example of chlorate manufacture, it has been estimated that, at high current densities, up to 60% of the space between the electrodes may be occupied by bubbles, increasing the cell voltage by ca. 0.6 V.

[004] As a result of these and other issues, new means of facilitating electrochemical transformations involving gases and liquids, and that avoid or diminish the energy and

electrical penalties associated with the presence of gas bubbles in liquid electrolytes, are of interest.

[005] One option is to entirely substitute the liquid-phase electrolyte with a suitable solid-state ion-exchange membrane that can carry an ion current between the electrodes. In this way, the problems associated with voidage, the bubble curtain effect and the bubble overpotential that occur when a liquid phase electrolyte is present between the electrodes, may be avoided or, at least, mitigated. Numerous patents teach of this technique. Typically, such solid-state ion-exchange membranes take the form of a Proton Exchange Membrane (PEM), which allows for electrically-induced transport between opposing electrodes of H^+ ions, or anion exchange membranes, which provide for transport of OH^- ions between opposing electrodes.

[006] The use of solid-state ion exchange membranes has its own technical problems however, often related to: (i) the relatively high electrical resistance created by placing such a material between the electrodes – high electrical resistance typically results in lower overall energy efficiency, and (ii) the need to still have water present (since water is required to facilitate the ion transport) without the formation of a bulk liquid phase in or about the resin (since such “flooding” effectively recreates the problems that are sought to be avoided). In such devices water is therefore often provided in the form of vapour at elevated temperatures, necessitating the addition of complex equipment to ensure the maintenance at all times of suitable and correct humidity levels.

[007] To illustrate the effects of these issues, one may consider the example of electrochemical cells that facilitate water electrolysis.

[008] Electrolyzers are devices that electrochemically convert water to hydrogen gas at the cathode and oxygen gas at the anode. A common class of this cell is a conventional alkaline electrolyzer, which employs a strongly alkaline liquid-phase electrolyte (typically 6 M KOH) between the cathode and anode. An ion-permeable, gas impermeable (or somewhat permeable) separator or diaphragm is typically employed between the two electrodes to prevent bubbles of hydrogen formed at the

cathode from mixing with bubbles of oxygen formed at the anode. Mixtures of hydrogen and oxygen are explosive and therefore an undesired safety hazard.

[009] The separator must also prevent the phenomenon of gas ‘crossover’, where hydrogen formed at the cathode passes through the separator to contaminate the oxygen formed at the anode, and oxygen formed at the anode passes through the separator to contaminate the hydrogen formed at the anode. If these contaminants approach the lower or higher explosion limits of hydrogen in oxygen, then a safety issue will have been created.

[010] Crossover may occur by two mechanisms: (i) a process whereby microbubbles of one or both of the gases lodge in the pores of the separator, thereby creating a gaseous pathway between the catholyte and anolyte chambers, and (ii) the migration of dissolved gases in the liquid electrolyte between the electrodes (through the separator).

For current separators, mechanism (i) may become a serious problem if the separator and its pores are not kept scrupulously wetted and free of gas bubbles at all times. This is particularly difficult to do at high applied pressures.

[011] To avoid or minimize the voidage and bubble-curtain effects, conventional alkaline electrolyzers typically continuously pump the 6 M KOH liquid electrolyte through the catholyte and anolyte chambers in order to sweep the gas bubbles away and keep the electrical conduction pathway between the anode and cathode as clear and void-free as possible. Despite these measures however, conventional alkaline electrolyzers can typically be efficiently operated only up to current densities of ca. 300 mA/cm² (at potentials near 2 V), with system efficiencies near 60%. At higher current densities the losses in efficiency due to bubbles in the liquid electrolyte become too severe.

[012] This compares with solid state proton exchange membrane (PEM) electrolyzers that typically operate at a current density of 1800 mA/cm², with efficiencies of up to 75%. Proton exchange membrane (PEM) electrolyzers are distinct from conventional alkaline electrolyzers in that they do not have a liquid phase electrolyte between the electrodes. Instead, they have a suitable solid-state ion-exchange resin, in the form of a

membrane, between the electrodes and operate at relatively high temperatures, where the water is present largely in the form of vapour and resin-bound water rather than as a separate, clearly identifiable liquid phase. In this way, solid state proton exchange membrane (PEM) electrolyzers, more or less, avoid the difficulties noted above, arising from voidage, the bubble curtain effect and the bubble overpotential that occur when a liquid phase electrolyte is employed between the electrodes.

[013] The presence of a liquid phase electrolyte between the electrodes in a gas-liquid electrochemical cell may have other highly deleterious effects. One example in this respect is that many gas generating liquid-filled electrochemical cells, like conventional alkaline electrolyzers, cannot handle sudden and large increases in current as may occur when they are electrically driven by intermittent power sources, like wind generators or solar panels, which produce highly intermittent and/or fluctuating current supplies. Currents of this type are typically produced by renewable energy sources.

[014] In the case of a very rapid rise in current, a large amount of gas may be produced very quickly in such cells, creating a potential pressure burst hazard and also potentially forcing the liquid electrolyte out of the cell, thereby damaging the cell either mechanically, or electrochemically, or both. Where porous electrodes have been used, it may also be imperative to avoid sudden, large-scale gas evolution in the pores since the formation of bubbles in this way can mechanically damage the catalyst, causing crumbling or erosion of the catalyst particles. There are various other ways in which a cell may be damaged by a sudden current surge. As alluded to earlier, conventional alkaline electrolyzers must therefore typically be operated at current densities of about 300 mA/cm² with surges in current or current density limited to no more than ca. 20-30% of the operational current.

[015] Similar problems arise in other electrochemical devices that employ liquid-electrolyte or gel-electrolyte in which gas bubbles may be formed. For example, many conventional batteries containing liquid-electrolyte or gel-electrolyte may form unwanted gas bubbles when they are being charged and, particularly, if they are overcharged. Such gas bubbles may damage the batteries by creating non-conducting voids within the electrical conduction pathway that increases the cell resistance and

therefore decreases the output efficiency of the battery. Such bubbles may also create pressure burst, electrolyte leak and other hazards. To avoid these problems, numerous patents teach methods and procedures by which to cut liquid-filled or gel-filled cells off from an electrical supply when bubble formation arises. For example, US20140120388
5 teaches of a cut-off switch for a battery during recharging where the activation of the cut-off switch is linked to the pressure of any gas that may be produced. US20120181992 teaches of a cut-off switch that is linked to the voltage of a battery connected to an intermittent source of energy. US20110156633 teaches of a solar power system that modulates the voltage of the incoming, intermittent current, in order
10 to avoid damage.

[016] By contrast, solid state proton exchange membrane (PEM) water electrolyzers are better able to handle sudden current surges, for the reason that the water to be split into hydrogen and oxygen is present largely in the form of vapour and resin-bound
15 water rather than as a separate, clearly identifiable liquid phase. Nevertheless, it is generally problematic to have sudden large increases in gas formation, with an accompanying increase in gas pressure at the ion-exchange membrane since gas crossover may increase and become an issue. That can be dealt with by using a thicker ion-exchange membrane. However, as noted by the authors of the presentation for
20 project PD117 in the 2015 Annual Merit Review Proceedings (Hydrogen Production and Delivery) of the US Department of Energy, even for PEM electrolyzers, it is generally “*Not possible to have high efficiency at high pressures with current membranes*”, since thicker separators provide greater resistance to current flow, thereby diminishing the electrical and energy efficiency. That is, even in the case where a
25 liquid-phase electrolyte has been replaced by a solid-state ion-exchange membrane between the electrodes, energy efficiencies are not necessarily substantively improved.

[017] While advances have been made in eliminating or minimising energy losses and inefficiencies in electrochemical cells, such as the effect that bubbles may have, still
30 further improvements are always desirable.

[018] In summary, there is a need to develop electrochemical cells and/or methods of operation capable of efficient operation under conditions of intermittent and/or

fluctuating currents. As a result of these and other issues, new or improved cells, devices and/or methods of facilitating electrochemical transformations involving gases and liquids, or gels, and that avoid, ameliorate or diminish energy and electrical penalties are of interest.

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[019] The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that the prior publication (or information derived from it) or known matter forms part of the common general
10 knowledge in the field of endeavour to which this specification relates.

SUMMARY

[020] This Summary is provided to introduce a selection of concepts in a simplified
15 form that are further described below in the Examples. This Summary is not intended to identify all of the key features or essential features of the claimed subject matter, nor is it intended to be used to limit the scope of the claimed subject matter.

[021] In various aspects there are provided electrochemical cells and methods of
20 operation or use under conditions of intermittent and/or fluctuating currents.

[022] In one aspect there is provided a method for operating an electrochemical cell, wherein the electrochemical cell comprises: a gas-producing electrode; a counter electrode, the gas-producing electrode and the counter electrode being separated by an
25 electrolyte. Preferably there is also provided one or more void volumes. The method comprises: supplying an intermittent and/or fluctuating current to at least the gas-producing electrode; and producing a gas at the gas-producing electrode as a result of an electrochemical reaction. Preferably the gas is received by the one or more void volumes.

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[023] In another aspect there is provided an electrochemical cell for producing a gas from an electrochemical reaction, comprising: a gas-producing electrode; a counter electrode; an electrolyte between the gas-producing electrode and the counter electrode;

and, preferably though optionally, one or more void volumes. In operation or use an intermittent and/or fluctuating current is supplied to at least the gas-producing electrode. Preferably the gas is produced at the gas-producing electrode and is received by the one or more void volumes.

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[024] Preferably, the electrolyte is a liquid electrolyte or the electrolyte is a gel electrolyte. Also preferably, there are no bubbles of the gas formed or produced, or there are substantially no bubbles of the gas formed or produced, at the gas-producing electrode.

10

[025] In example embodiments, “substantially free of bubble formation” or “substantially bubble-free” or “substantially no bubbles” means that less than 15% of the gas produced takes the form of bubbles in the electrolyte. In another example embodiment, less than 10% of the gas produced takes the form of bubbles in the electrolyte. In other example embodiments, less than 8%, less than 5%, less than 3%, less than 2%, less than 1%, less than 0.5%, or less than 0.25%, of the gas produced takes the form of bubbles in the electrolyte.

15

[026] In one example the current is produced by an intermittent and/or fluctuating power source. In another example the power source is a solar-generator or a wind-generator or an ocean wave/tidal-generator of electricity. In another example the current is unconditioned. In another example the current is derived from excess electrical energy from an electrical grid.

20

[027] In another example there is no ion-exchange membrane positioned between the gas-producing electrode and the counter electrode. In another example there is no diaphragm (e.g. separator) positioned between the gas-producing electrode and the counter electrode.

25

[028] In another example the gas-producing electrode is a gas diffusion electrode. In another example the counter electrode is a gas diffusion electrode. The counter electrode may produce a second gas and bubbles of the second gas are not formed or produced, or are substantially not formed or produced at the counter electrode.

30

Optionally, the second gas is received by separate one or more void volumes. In another example the current fluctuates by more than double the current.

[029] In another example the one or more void volumes are positioned within, partially within or adjacent to the electrolyte. In another example the one or more void volumes are positioned at or adjacent to the gas-producing electrode. In another example the one or more void volumes form a gaseous conduit to transport the gas. In another example the one or more void volumes allow the gas if formed rapidly in the electrolyte to escape from the electrochemical cell.

10

BRIEF DESCRIPTION OF THE FIGURES

[030] Illustrative embodiments will now be described solely by way of non-limiting examples and with reference to the accompanying figures. Various example embodiments will be apparent from the following description, given by way of example only, of at least one preferred but non-limiting embodiment, described in connection with the accompanying figures.

15

[031] Figure 1 schematically depicts an example liquid-gas electrochemical cell that can be utilised in present embodiments (not to scale).

20

[032] Figure 2 schematically depicts the options available to gas formed at or near to the liquid-gas interface in an electrochemical cell.

25 [033] Figure 3 illustrates an example method for operating an electrochemical cell.

[034] Figure 4 schematically depicts a first example arrangement for voids in a liquid-gas electrochemical cell.

30 [035] Figure 5 schematically depicts a second example arrangement for voids in a liquid-gas electrochemical cell.

[036] Figure 6 schematically depicts an example electrolyzer, including two gas diffusion electrodes and whose standard operating current is 10 mA.

[037] Figure 7 depicts an example current profile that rapidly and repeatedly fluctuates very suddenly between a current of 5 mA and a current of 250 mA.

- 5 [038] Figure 8 depicts an example variation in the voltage at each of the points marked A-D in Figure 7, measured at precisely the same time each day, over a period of 55 days of continuous operation.

DETAILED DESCRIPTION AND EXAMPLES

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[039] The following modes, features or aspects, given by way of example only, are described in order to provide a more precise understanding of the subject matter of a preferred embodiment or embodiments.

15 Example Electrochemical Cells and Methods of Operation

- [040] International Patent Publication No. WO2013/185170 for "Gas Permeable Electrodes and Electrochemical Cells" filed 11 June 2013, is incorporated herein by reference, and describes gas diffusion electrodes, including various alkaline and acidic
20 electrolyzers and including gas-producing electrodes, and aspects thereof, which can be spiral-wound or kept in "flat-sheet" format, and utilised in the present examples.

- [041] Further aspects and details of example cells, modules, structures and electrodes, including gas-producing electrodes, and methods of operation, that are incorporated
25 herein by reference, and that can be utilised in the present examples are described in the Applicant's previously filed International Patent Publication No. WO2015/013766 for "Modular Electrochemical Cells" filed 30 July 2014; the Applicant's previously filed International Patent Publication No. WO2015/013765 for "Composite Three-Dimensional Electrodes and Methods of Fabrication" filed 30 July 2014; the Applicant's
30 previously filed International Patent Publication No. WO2015/013767 for "Electro-Synthetic or Electro-Energy Cell With Gas Diffusion Electrode(s)" filed on 30 July 2014; the Applicant's previously filed International Patent Publication No. WO2015/013764 for "Method and Electrochemical Cell for Managing Electrochemical

Reactions" filed on 30 July 2014; the Applicant's previously filed International Patent Publication No. WO2015/085369 for "Electrochemical Cells and Components Thereof" filed on 10 December 2014; and in the Applicant's concurrent International Patent Applications entitled "Electrochemical cell and components thereof capable of
5 operating at high current density" and "Electrochemical cell and components thereof capable of operating at high voltage", filed on 14 December 2016, which are all incorporated herein by reference.

[042] The electrodes, electrochemical cells and/or methods of operation described in
10 the above patent applications can be used in present embodiments.

[043] Referring to Figure 1 there is illustrated a non-limiting example of an electrochemical cell 10. The electrochemical cell 10 includes an electrolyte 15, preferably a liquid electrolyte or a gel electrolyte that can be subjected to an electrolyte
15 pressure, existing between and/or about anode 20 and cathode 30, i.e. electrodes 20, 30. The anode 20 can be a gas-producing electrode and/or the cathode 30 can be a gas-producing electrode. Either of the anode 20 or the cathode 30 can be termed a counter electrode respective to the other electrode. For example, there can be provided an electrode 20 and a counter electrode 30, or an electrode 30 and a counter electrode 20.
20 Optionally, on, embedded in, or close to the surface of the electrodes 20, 30 is a conductive layer or region containing a suitable catalyst(s). Preferably, the electrode and catalyst layers at the anode 20 and cathode 30 are permeable to gases. The electrochemical cell 10 includes a housing or container 40 for containing electrolyte 15. First gas region, channel or conduit 50 is formed as part of, adjacent or next to anode
25 20, for collecting and/or transporting a first gas 70, if any, produced at anode 20. Second gas region, channel or conduit 60 is formed as part of, adjacent or next to cathode 30, for collecting and/or transporting a second gas 80, if any, produced at cathode 30. First gas region, channel or conduit 50 and second gas region, channel or conduit 60 can be provided separately or together in electrochemical cell 10. Depending
30 on the particular reaction, first gas 70 and/or second gas 80 can be produced, and optionally transported out of electrochemical cell 10. The direction of gas exit is for illustration only and can be varied.

[044] First gas region, channel or conduit 50 provides one example form of one or more void volumes, positioned at or adjacent to electrode 20. Second gas region, channel or conduit 60 also provides one example form of a separate one or more void volumes, positioned at or adjacent to electrode 30.

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[045] An electrical current, having an associated current density, is applied to the electrodes 20, 30 or a voltage can be applied across electrodes 20, 30 using an electrical power source. No bubbles, or substantially no bubbles, of first gas 70 and/or second gas 80 are formed at either the anode 20 or cathode 30 surfaces. That is, the electrochemical cell is substantially free of bubble formation, i.e. substantially bubble-free, at the anode and/or the cathode. This means that less than 15% of the gas formed or produced at the anode and/or the cathode takes the form of bubbles in the electrolyte. In a particular example, the anode 20 and/or cathode 30 can include a porous conductive material, which can be flexible. Preferably, the porous conductive material is gas permeable and liquid permeable (i.e. electrolyte permeable). The anode 20 and/or cathode 30 can include, or be next to, fixed to, or adjacent, a gas permeable material, which also can be flexible. Preferably, the gas permeable material is gas permeable and liquid impermeable (i.e. electrolyte impermeable), and thus the anode 20 and/or cathode 30 composite structure can be gas permeable and liquid impermeable (i.e. electrolyte impermeable), and optionally flexible. Preferably, the gas permeable material is non-conductive. The anode 20 and/or cathode 30 can be Gas Diffusion Electrodes (GDEs). In an optional example, electrolyte 15 can be pumped past the electrodes 20, 30 using a pump. In other example embodiments, less than 10% of the gas produced takes the form of bubbles in the electrolyte. In other example embodiments, less than 8%, less than 5%, less than 3%, less than 2%, less than 1%, less than 0.5%, or less than 0.25%, of the gas produced takes the form of bubbles in the electrolyte.

[046] Reference to a gas permeable material should be read as a general reference including any form or type of gas permeable medium, article, layer, membrane, barrier, matrix, element or structure, or combination thereof.

[047] Reference to a gas permeable material should also be read as including any medium, article, layer, membrane, barrier, matrix, element or structure that is

penetrable to allow movement, transfer, penetration or transport of one or more gases through or across at least part of the material, medium, article, layer, membrane, barrier, matrix, element or structure (i.e. the gas permeable material). That is, a substance of which the gas permeable material is made may or may not be gas permeable itself, but

5 the material, medium, article, layer, membrane, barrier, matrix, element or structure formed or made of, or at least partially formed or made of, the substance is gas permeable. The gas permeable material may be porous, may be a composite of at least one non-porous material and one porous material, or may be completely non-porous. The gas permeable material can also be referred to as a "breathable" material. By way

10 of clarifying example only, without imposing any limitation, an example of a gas permeable material is a porous matrix, and an example of a substance from which the gas permeable material is made or formed is PTFE.

[048] An electrode can be provided by or include a porous conductive material.

15 Preferably, the porous conductive material is gas permeable and liquid permeable.

[049] Reference to a porous conductive material should be read as including any medium, article, layer, membrane, barrier, matrix, element or structure that is penetrable to allow movement, transfer, penetration or transport of one or more gases

20 and/or liquids through or across at least part of the material, medium, article, layer, membrane, barrier, matrix, element or structure (i.e. the porous conductive material). That is, a substance of which the porous conductive material is made may or may not be gas and/or liquid permeable itself, but the material, medium, article, layer, membrane, barrier, matrix, element or structure formed or made of, or at least partially formed or

25 made of, the substance is gas and/or liquid permeable. The porous conductive material may be a composite material, for example composed of more than one type of conductive material, metallic material, or of a conductive or metallic material(s) and non-metallic material(s).

30 [050] By way of clarifying examples only, without imposing any limitation, examples of porous conductive materials include porous or permeable metals, conductors, meshes, grids, lattices, cloths, woven or non-woven structures, webs or perforated sheets. The porous conductive material may also be a material that has "metal-like"

properties of conduction. For example, a porous carbon cloth may be considered a porous conductive material since its conductive properties are similar to those of a metal.

5 [051] The porous conductive material may be a composite material, for example composed of more than one type of conductive material, metallic material, or of a conductive or metallic material(s) and non-metallic material(s). Furthermore, the porous conductive material may be one or more metallic materials coated onto at least
10 onto at least part of a separate gas permeable material that is used in association with the gas permeable material. By way of clarifying examples only, without imposing any limitation, examples of porous conductive materials include porous or permeable metals, conductors, meshes, grids, lattices, cloths, woven or non-woven structures, webs or perforated sheets. The porous conductive material may be a separate
15 material/layer attached to the gas permeable material, or may be formed on and/or as part of the gas permeable material (e.g. by coating or deposition).

[052] The electrochemical cell can be provided in a “flat-sheet” (i.e. stacked) or a “spiral-wound” format. Flat-sheet means the electrodes (e.g. cathodes and/or anodes)
20 are formed of planar layers or substantially planar layers, so that a flat-sheet electrochemical cell is comprised of a plurality of planar electrodes or substantially planar electrodes. A flat-sheet electrochemical cell can be stacked together with other flat-sheet electrochemical cells (one on top of another in a series or array of electrochemical cells) to form a layered stack of multiple electrochemical cells (i.e. a
25 stacked electrochemical cell). The “flat-sheet” and “spiral-wound” cells, modules or reactors typically involve gas permeable, liquid impermeable gas diffusion electrode sheets or layers stacked in two or more layers, where the electrodes, including gas-producing electrodes, are separated from one another by spacers or spacer layers, for example distinct electrolyte channel spacers (which are permeable to, and intended to
30 guide the permeation of liquid electrolyte through the cell) and/or gas channel spacers (which are permeable to, and intended to guide the permeation of gases through the cell). There may be more than one type of gas channel. For example, there may be two distinct gas channels, one for a first gas (e.g. hydrogen in a water electrolysis cell) and

another for a second gas (e.g. oxygen in a water electrolysis cell). There may, similarly, be separate channels for more than one electrolyte. For example, in a modified chlor-alkali cell suitable for manufacturing chlorine - hypochlorite disinfection chemistries, there may be separate channels for the feed electrolyte (NaCl solution, 25%, pH 2-4) and the product electrolyte.

[053] In the “spiral-wound” arrangement, the resulting multi-electrode stack is tightly wound about a core element, to thereby create the spiral-wound cell or module. The core element may contain some or all of the gas-liquid and electrical conduits with which to plumb and/or electrically connect the various components of the cell or module. For example, the core element may combine all of the channels for one or another particular gas in the stack into a single pipe, which is then conveniently valved for attachment to an external gas tank. The core element may similarly contain an electrical arrangement which connects the anodes and cathodes of the module into only two external electrical connections on the module – a positive pole and a negative pole.

[054] One key advantage of spiral-wound cells or modules over other module arrangements is that they provide a high overall electrochemical surface area within a relatively small overall geometric footprint. A spiral-wound electrochemical module is believed to provide for the highest possible active surface area within the smallest reasonable footprint. Another advantage of spiral-wound arrangements is that round objects are easier to pressurize than other geometries which involve corners. So, the spiral design has been found to be beneficial for electrochemical cells in which the electrochemical reaction is favourably impacted by the application of a high pressure.

[055] Regardless of whether the reactor or cell arrangement is spiral wound or flat sheet the modular reactor units may be so engineered as to be readily attached to other identical modular units, to thereby seamlessly enlarge the overall reactor to the extent required. The combined modular units may themselves be housed within a second, robust housing that contains within it all of the liquid that is passed through the modular units and which serves as a second containment chamber for the gases that are present within the interconnected modules. The individual modular units within the second, outer robust housing may be readily and easily removed and exchanged for other,

identical modules, allowing easy replacement of defective or poorly operational modules.

Minimising Gas Solubility and Bubble Formation

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[056] In example embodiments, methods and cells for facilitating the operation of electrochemical cells by minimising gas solubility and bubble formation are described in the Applicant's concurrent International Patent Application for "Methods of improving the efficiency of gas-liquid electrochemical cells", filed on 14 December 10 2016, which is incorporated herein by reference.

[057] The inventors have realised that in electrochemical cells involving a liquid or gel electrolyte between the electrodes, which are preferably one or more gas-producing electrodes, gas that may be formed or built up within the liquid electrolyte in the cell 15 (for example, at the surface of an electrode in the cell) can do one of three things:

- (1) The gas can dissolve in the liquid electrolyte and migrate away;
- (2) The gas can form a new, independent bubble;
- (3) The gas can join an existing bubble (or gas region), either natural or 20 man-made. That is, the gas can pass across an existing gas-liquid interface into an existing gaseous phase or region.

[058] Figure 2 illustrates, in schematic form, the three different pathways 1, 2, 3, following the above numbering, available to gas formed within a liquid electrolyte in a 25 gas-liquid cell.

[059] Pathway (1) above is generally deleterious to energy efficiency, since the presence of dissolved gases in the liquid electrolyte between the electrodes of an electrochemical cell leads to higher electrical resistance, as taught in US 20080160357. 30 It also promotes crossover between the electrodes.

[060] For the reasons given in the Background section, pathway (2) above is generally also deleterious to the efficient operation of a cell having liquid or gel electrolyte between its electrodes.

5 [061] The inventors have, contrary to known expectations, realised that pathway (3) above need not be deleterious to the efficient operation of a cell having liquid or gel electrolyte between the electrodes, if the “existing bubble” (i.e. “gas region” or “one or more void volumes”), either natural or man-made, lies outside of, or substantially outside of, the conduction pathway between the electrodes.

10 [062] One or more “void volumes” can be provided by one or more porous structures, which can be provided by one or more gas permeable materials. The one or more porous structures, or gas permeable materials, providing one or more void volumes, are preferably gas permeable and liquid impermeable, or substantially liquid impermeable.

15 The one or more porous structures, or gas permeable materials, providing one or more void volumes, are also preferably non-conducting.

[063] The inventors have realised that, in fact, pathway (3) provides a potentially useful means of controlling and handling gas formation in a manner that ensures gas

20 formation is not deleterious to the operation and efficiency of the cell. That is, the inventors have unexpectedly realised that instead of seeking to suppress or block bubble formation, it may be more efficacious to direct gas formation to a pre-existing bubble or gas region (i.e. one or more void volumes), either natural or man-made, that has been designed to accept and accommodate gas formation in a way that does not impinge or

25 substantially impinge on the operation and efficiency of the cell.

[064] Moreover, the inventors have realised that, as a consequence of the Laplace equation, it is, in fact, energetically more favourable for newly formed or dissolved gas within a liquid to join a large, pre-existing bubble or gas region, either natural or man-

30 made, than it is for the gas to form an independent, new bubble on a surface (either within a ‘cleft’ or as a stand-alone spherical bubble). This is because a large, pre-existing bubble (which could also be considered as a gas region or a void volume) will

necessarily have a larger radius and therefore a lower internal ('Laplace') pressure than either a newly-formed spherical bubble or a newly-formed bubble in a surface 'cleft'.

[065] Furthermore, the concentration of dissolved gas within a liquid electrolyte is also necessarily minimised about a pre-existing bubble, gas region or void volume, either natural or man-made, since the bubble, region or volume provides an additional interface through which excess gaseous molecules are favoured to escape the liquid phase. In particular, it is, effectively, impossible for a liquid electrolyte to become supersaturated near to such a bubble, since the bubble interface provides a ready route for the excess gas to escape the liquid phase. This is important because the lower the quantity of dissolved gases in the liquid electrolyte, the lower its electrical resistance and the greater the energy / electrical efficiency of the cell, whilst crossover is also suppressed.

[066] Thus, in particular example embodiments, the inventors have realised that providing one or more void volumes, e.g. a pre-existing bubble, gas region or gas pathway, either naturally occurring or man-made, that is preferably positioned outside of the electrical conduction pathway between a gas-producing electrode and its counter electrode, substantially outside of the electrical conduction pathway between a gas-producing electrode and its counter electrode, partially outside of the electrical conduction pathway between a gas-producing electrode and its counter electrode, peripheral to or adjacent to the electrical conduction pathway between a gas-producing electrode and its counter electrode, and/or having a small cross-sectional area relative to the electrical conduction pathway between a gas-producing electrode and its counter electrode, and which can be within, partially within, adjacent to or near to a liquid electrolyte, or gel electrolyte, between the gas-producing electrode and its counter electrode of a cell, has the effect of not only disfavouring pathway (2) above but also minimising pathway (1) above. In another example, the counter electrode is a gas-producing counter electrode, so that both of the electrodes are gas-producing electrodes.

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[067] In particular example embodiments, the inventors have, further, discovered that pathway (1) above may be further lessened by selecting physical conditions for the cell that diminish, reduce, or minimise the dissolution of gases and/or their diffusion in the

liquid electrolyte under conditions of high, higher, or maximal electrolyte conductivity. Stated differently: in particular example embodiments the inventors have discovered that the deleterious effect of pathway (1) on the cell may be further lessened by configuring or selecting physical conditions for the cell that diminish, reduce, or
5 minimise the effect that dissolved gases may have on the operation of the cell under conditions of high, higher, or maximal energy efficiency. The physical conditions include but are not limited to, one or more of the following:

- a. The temperature of operation;
- 10 b. The type and concentration of the electrolyte in the liquid phase (including the surface tension of the electrolyte);
- c. The pressure applied to the liquid electrolyte (including the pressure differential across a gas diffusion electrode that may be used);
- 15 d. The nature of any spacer that may be used to separate the electrodes;
- e. The mode of operation;
- f. The flow-rate of the liquid electrolyte; and
- g. The flow-type of the liquid electrolyte (i.e. laminar or turbulent
20 flow).

[068] In particular example embodiments, the inventors have found that it may be beneficial to use physical laws such as Ficks' law, Henry's law, Raoult's law, the Senechov equation, the Stokes-Einstein (-Sutherland) equation, and similar expressions,
25 to guide the setting of the above physical conditions. It may be useful to thereafter further refine the settings for the physical conditions using empirical measurement.

[069] In particular example embodiments, the inventors have found that, in general and without limitation, the physical conditions within the cell should be configured or
30 selected so as to:

- (I) increase or maximise the electrical conductance of the electrolyte (typically, but not exclusively in units of S/cm) to the greatest reasonable extent,

- (II) whilst simultaneously reducing or minimising the dissolution of gases in the electrolyte (typically, but not exclusively in units of mol/L) to the greatest reasonable extent, and
- (III) reducing or minimising the rate of diffusion of the dissolved gas or gases in the electrolyte (typically, but not exclusively in units of cm^2/s) to the greatest reasonable extent.

[070] For convenience, (I) above is referred to as the “Conduction Factor” and given the symbol CF. In general, the physical conditions employed within the cell should be such that CF (typically, but not exclusively in units of S/cm) is increased or maximised to the greatest reasonable extent. The conductance, or conductivity of the electrolyte, is the reciprocal of electrical resistivity (in $\Omega \text{ cm}$ – ohm centimeters). Therefore the Conduction Factor, or conductivity, is used as a measure the ionic conductance of the electrolyte. The unit of measurement used is typically, but not exclusively a Siemen per centimetre (S/cm).

[071] For convenience, the product of (II) multiplied by (III) above is referred to as the “Gas Dissolution and Diffusion Factor” and given the symbol GDDF. In particular example embodiments, the inventors have found that, in general and without limitation, the physical conditions employed within the cell should be such that GDDF (typically, but not exclusively in units of: $\text{cm}^2 \cdot \text{mol}/\text{L} \cdot \text{s}$) is reduced or minimised to the greatest reasonable extent. Where multiple gases are involved, the sum of their GDDF’s should be minimised to the greatest reasonable extent.

[072] The expression for GDDF derives from Ficks’ law for diffusion of dissolved gases in a liquid phase, and reflects the influence that diffusing, dissolved gases may have on the chemical processes present in an electrochemical cell of the present embodiments. The lower GDDF is, the less influence dissolved gases may have. That is, the lower GDDF is, the smaller is the effect of pathway (1) above, or the smaller is the influence of pathway (1) above on the chemical reactions in an electrochemical cell of the present embodiments.

[073] For convenience, the ratio of CF divided by GDDF is referred to as the “Electrolyte Factor” and given the symbol EF. In general and without limitation, in particular example embodiments, the inventors have found that the physical conditions employed within the cell should be such that EF (typically, but not exclusively in units of: $\text{L s} / \Omega \text{ cm}^3 \text{ mol}$) is increased or maximised to the greatest extent reasonable.

[074] The expression $\text{EF} = \text{CF}/\text{GDDF}$ reflects the ratio of the electrically conductive capacity of the liquid electrolyte to the extent of gas dissolution and diffusion in the liquid electrolyte. As noted above, in particular example embodiments, the inventors have found that certain electrochemical cells operate most efficiently if the electrical conductance of the liquid electrolyte is increased or maximised whilst simultaneously the extent of gas dissolution and diffusion in the liquid electrolyte is reduced or minimised.

[075] Once the above combination of factors have been realised by setting the physical conditions in the most suitable, or least compromised manner, then features of the electrochemical cell design may be altered, set, created, or implemented to realise additional energy efficiencies. The electrochemical cell design features include but are not limited to, one or more of the following:

- a. The inter-electrode distance employed;
- b. The current density employed.

[076] For convenience, the Inter-electrode Distance (typically, but not exclusively in units of: cm) is given the symbol ID, while the Current Density (typically, but not exclusively in units of: mA/cm^2) is given the symbol CD.

[077] In particular example embodiments, the inventors have found that, in general and without limitation, the features of design within the cell, namely: the Inter-electrode Distance (ID; typically, but not exclusively in units of: cm) and the Current Density (CD; typically, but not exclusively in units of: mA/cm^2) should be set such that the product of the square of CD (typically, but not exclusively in units of: mA/cm^2) multiplied by ID (typically, but not exclusively in units of: cm) and divided by CF (typically, but not exclusively in units of: S/cm), is reduced or minimized to the greatest

reasonable extent. For convenience, this expression, $((CD)^2 \times ID) / CF$, is referred to as the “Power Density Factor” and given the symbol PF (typically, but not exclusively in units of $mA^2 \cdot \Omega / cm^2$). In general and without limitation, the physical conditions employed within the cell should be such that PF is reduced or minimized to the greatest

5 reasonable extent.

[078] Thus, the Power Density Factor (PF) is given by:

$$PF = ((CD)^2 \times ID) / CF.$$

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[079] The Power Density Factor (PF) is related to the rate at which work must be done to push an electrical current between the electrodes in the electrochemical cell – i.e. the electrical power consumed per unit area of gas-producing electrode. An increased energy and electrical efficiency in the cell must necessarily be accompanied by a

15 reduction or minimization in the rate of work that must be done to drive an electric current between the electrodes in the cell. The quantity PF is therefore a proxy for, and inversely related to the energy efficiency of the cell.

[080] In particular example embodiments, the inventors have found that it is also

20 useful to quantify the percentage of the gases generated in an electro-synthetic cell of present embodiments, that crossover from one electrode to the other due to gas migration in the liquid electrolyte. This Crossover quantity, CO, as a percentage, is provided by the expression for Crossover (CO):

$$25 \quad CO = (n \cdot F \cdot GDDF) / (ID \cdot CD) \times 100 \quad (\text{in units of: \%})$$

where,

n = the number of electrons exchanged in the balanced, electrochemical half-reaction occurring at the gas-producing electrode in question (i.e. the number of

30 electrons in the balanced redox half-reaction),

F = the Faraday constant = 96,485 Coulombs / mol,

GDDF = Gas Dissolution and Diffusion Factor, which equates to:

= (concentration of dissolved gas [in units of: mol/L]) x (rate of diffusion of the dissolved gas [in units of: cm²/s])

(in overall units of: cm².mol/L.s,

which can also be expressed as: mol / (1000 cm s),

5 ID = the inter-electrode distance (in units of: cm),

CD = the current density (in units of: mA/cm²), and

where the individual factors in the above equation have the following units:

($n \cdot F \cdot \text{GDDF}$) has units: C.cm² / L.s,

which can also be expressed as: C / (1000 cm s),

10 which can also be expressed as: mA / cm

($n \cdot F \cdot \text{GDDF}$)/ID has units: mA / cm²

CD has units: mA / cm²

($n \cdot F \cdot \text{GDDF}$)/(ID . CD) x 100 has units: %

15 [081] In particular example embodiments, the inventors have found that, in general and without limitation, substantial energy efficiencies which may be greater than those achievable using other approaches, can be realised in electrochemical cells if the physical conditions in the cell and the features of cell design within the cell are set so that:

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- The Electrolyte Factor, EF (in units of: L s / Ω cm³ mol), is increased or maximised to the greatest reasonable extent;

- The Power Density Factor, PF (in units of: mA² Ω / cm²), is reduced or minimized to the greatest reasonable extent; and

25 - The Crossover, CO (in %), is reduced or minimized to the greatest reasonable extent.

[082] Taking all of the above into account, in particular example embodiments, the inventors further realised that when the effect of a careful selection of the physical conditions and the cell design features as described above, are combined with the effect of providing an existing bubble or gas region, i.e. one or more void volumes, either natural or man-made, that lies outside of, or substantially outside of the electrical conduction pathway, or positioned to have only a small or minimal effect between the

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electrical conduction pathway, then significant improvements in energy efficiencies are achieved in the electrochemical cell. These energy efficiencies may be greater than those achievable using other approaches, such as the use of solid-state ion-exchange membranes between the electrodes.

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Type of liquid-gas electrochemical cell	Example	Voltage drop between the electrodes under typical operating conditions*
Cell with liquid electrolyte where gas is generated in the form of bubbles	Conventional alkaline electrolyzer	up to 0.600 V
Cell with a solid-state, ion-exchange membrane electrolyte, where gas is generated in the form of vapour	PEM electrolyzer	0.229 V
Cell with liquid electrolyte where gas joins a pre-existing bubble / gas region outside of the conduction pathway	Alkaline electrolyzer of present embodiments	0.011 V

*data from Example 4 in the Applicant's concurrent International Patent Application entitled "Methods of improving the efficiency of gas-liquid electrochemical cells", filed on 14 December 2016, and Example 2 in the Applicant's concurrent International Patent Application entitled "High pressure electrochemical cell", filed on 14 December 2016, both of which are incorporated herein by reference

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Table 1 compares the ohmic voltage drop that occurs during typical operation of a conventional alkaline electrolyzer, a PEM electrolyzer and an electrolyzer of present embodiments.

[083] Thus, for example, as noted in Table 1: an electrochemical cell in which gas is produced in the form of bubbles, such as a conventional alkaline electrolyzer, may experience a typical voltage drop of up to 0.6 V between the electrodes under operational conditions due to the effect of bubbles in the liquid electrolyte.

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[084] By contrast, a conventional PEM electrolyzer utilizing a solid-state Nafion 117 PEM membrane (185 μm thickness; immersed in water) between the electrodes and operating at a typical current density of 1.8 A/cm^2 at 80°C will experience a much smaller 0.229 V ohmic drop between the electrodes.

[085] Best of all, however, is an alkaline electrolyzer of the current embodiments having a 3 mm inter-electrode gap and operating at a typical current density of 50 mA/cm^2 at 80°C using aqueous 6 M KOH as a liquid electrolyte. Such an electrolyzer will experience a mere 0.011 V ohmic drop between the electrodes. A low voltage drop is consistent with high, or higher fundamental energy and electrical efficiency.

[086] It should be noted that, even if the PEM electrolyzer of the above example were to be operated at one-twentieth of its normal, operational current density (i.e. at 90 mA/cm^2), which would likely be economically unviable, it would still experience a higher voltage drop than that experienced by the above alkaline electrolyzer.

[087] Summarising these concepts, embodiments involve electrochemical cells and methods of use or operation in which one or more gas-producing electrodes operate in a manner that is bubble-free or substantially bubble-free. The electrochemical cell does not have a diaphragm present between the gas-producing electrodes. Preferably, the electrochemical cell makes use of a particular catalyst-electrolyte system. The electrochemical cell is optimised to determine the best settings for different variables of the electrochemical cell, including:

- (i) the electrolyte concentration (e.g. KOH concentration in one example);
- (ii) the temperature of the electrolyte;
- (iii) the pressure applied to the electrolyte;
- (iv) the inter-electrode distance (e.g. the distance between the anode and the cathode); and
- (v) the current density.

For optimisation of the electrochemical cell, it is required to determine what settings for these variables yield the optimum performance by a gas-producing electrode of the electrochemical cell.

[088] There are three main relationships between these variables that are believed to be critical to optimising electrode performance; these are, as described above: the Electrolyte Factor (EF), the Power Density Factor (PF) and the Crossover (CO). The maximum or optimal electrode performance occurs when the following conditions are simultaneously met:

EF is maximised,
PF is minimised and
CO is minimised.

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[089] Not only may the energy efficiencies realised by this approach be more substantial than those achievable using other approaches, such as the use of solid-state ion-exchange membranes between the electrodes, but they may also be most amplified under circumstances where energy losses are normally at their greatest in conventional cells; that is, at higher pressures and/or current densities.

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[090] Of the five different variables (i)-(v) listed above, three are physical reaction aspects - namely, (i) the electrolyte concentration, (ii) the temperature, and (iii) the pressure. However, the other two variables are, effectively, engineering quantities and can be set from wide ranges for satisfying or improving optimisation, namely: (iv) the inter-electrode distance, and (v) the current density.

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[091] That is important because the Electrolyte Factor (EF) is determined only by variables (i)-(iii) above, i.e. (i) the electrolyte concentration, (ii) the temperature, and (iii) the pressure. By contrast, the Power Density Factor (PF) and the Crossover (CO) are determined mainly by the engineering variables, being (iv) the inter-electrode distance, and (v) the current density.

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[092] In fact, the Power Density Factor (PF) is influenced in a minor way by one component of the Electrolyte Factor (EF), namely the Electrolyte Conduction Factor (CF), whereas the Crossover (CO) is influenced in a minor way by the other component of the Electrolyte factor (EF), namely the Gas Diffusion and Dissolution Factor (GDDF).

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[093] Thus, generally one is limited by nature and the laws of physics in where the Electrolyte Factor (EF) will peak. However, the Power Density Factor (PF) and the Crossover (CO) can be, effectively, determined or set for optimisation. In other words, one can find out where the Electrolyte Factor (EF) will peak, and then use the available control or freedom of the engineering quantities to cause the Power Density Factor (PF) and the Crossover (CO) to be simultaneously at minima (zeroed in the case of CO), or simultaneously as close to minima as possible.

[094] In particular example embodiments, the inventors have therefore discovered that energy savings can be realised in a liquid-gas electrochemical cell having a liquid- or gel-electrolyte between the gas-producing electrodes by:

(1) providing a large, pre-formed or pre-existing bubble or bubbles (i.e. void volume(s), or gas region, or gas pathway, or bubble region), either natural or man-made, within, at, adjacent to or near to the source of gas in the cell in order to:

- i. reduce or minimise gas dissolution in the liquid electrolyte, and
- ii. reduce or minimise independent bubble formation;

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(2) locating the pre-formed or pre-existing gas bubble(s) or region(s), either natural or man-made, outside of or on the periphery of the conduction pathway of the electrochemical cell, or to occupy only a small cross-sectional area within the conduction pathway of the electrochemical cell, so that its presence does not substantially increase the electrical resistance of the cell;

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and/or under circumstances where:

(3) the physical conditions within the cell and the cell design are set so that:

- i. the Electrolyte Factor (EF; for example in units of: $\text{L s} / \Omega \text{ cm}^3 \text{ mol}$) is increased or maximised to the greatest reasonable extent; and

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- ii. the Power Density Factor (PF; for example in units of: $\text{mA}^2 \Omega / \text{cm}^2$) and the Crossover (CO; for example %), are reduced or minimized to the greatest reasonable extent.

5 [095] In particular example embodiments, the inventors have further realised that not only can the energy efficiencies realised by this approach be more substantial than those achievable using other approaches, such as the use of solid-state ion-exchange membranes between the electrodes, but the energy efficiencies can also be most amplified under circumstances where energy losses are normally at their greatest in
10 conventional cells; that is, at higher pressures and/or current densities.

[096] In one example aspect, there is provided a liquid-gas electrochemical cell having a liquid- or gel-electrolyte between the gas-producing electrodes where:

15 (I) one or more void volumes, that lie outside of or on the periphery of the conduction pathway or occupy only a small cross-sectional area within the conduction pathway of the electrochemical cell, are located within, partially within, adjacent to, or near to the electrolyte; and where,

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(II) the physical conditions in the cell and the cell design are set so that:
i. the Electrolyte Factor (EF; in units of: $\text{L.s}/\Omega.\text{cm}^3.\text{mol}$) is increased or maximised to the greatest reasonable extent; and
ii. the Power Density Factor (PF; in units of: $\text{mA}^2.\Omega/\text{cm}^2$) and the
25 Crossover (CO; %), are reduced or minimized to the greatest reasonable extent.

[097] Preferably but not exclusively, the one or more void volumes are directly adjacent to, next to, or positioned within the source of gas formation, in order to
30 facilitate the migration of gas to the one or more void volumes. One or more “void volumes” can be provided by one or more porous structures, which can be gas permeable materials. The one or more porous structures, or gas permeable materials,

providing one or more void volumes, are preferably gas permeable and liquid impermeable, or substantially liquid impermeable.

5 [098] Preferably but not exclusively, the one or more void volumes are provided by a gas permeable material (i.e. a porous structure) that is not permeable to the electrolyte (i.e. liquid impermeable) but accommodates or allows passage of gas (i.e. gas permeable). Thus, in one preferred form, a void volume is provided by a gas permeable and liquid impermeable porous structure(s) or material(s). The one or more void volumes are preferably non-conductive.

10 [099] In the case of an aqueous liquid electrolyte, the one or more void volumes are preferably but not exclusively provided by a porous hydrophobic structure, such as a porous hydrophobic assembly, membrane or hollow fibre, or a collection of such structures, which remains unfilled with liquid electrolyte or gel electrolyte during the
15 operation of the cell.

[0100] The void volume, or the one or more void volumes, may be considered to be a “pre-existing bubble”, a “pre-formed bubble”, a “gas region”, a “gas pathway”, a “gas void”, an “artificial bubble” or a “man-made bubble”. Preferably the void volume, or
20 the one or more void volumes, lies outside of or on the periphery of the electrical conduction pathway of the cell, or occupies only a small cross-sectional area within the electrical conduction pathway. In another example, the cross-sectional area of the void volume is less than the cross-sectional area of the electrical conduction pathway, relative to a perpendicular direction extending from the surface of an electrode.

25 [0101] In alternative preferred embodiments, a void volume may be provided by a natural bubble or bubbles that are statically or near-statically positioned outside of, or within a small cross-sectional area in the conduction pathway of the cell. For example, the static or near-static, natural bubble or bubbles may be contained, or mechanically
30 trapped within an accommodating structure that is located outside of, or within a small cross-sectional area within the conduction pathway of the cell. In another example, the natural, static or near-static bubble or bubbles may simply be formed or located outside of, or within a small cross-sectional area in the conduction pathway of the cell.

[0102] In one preferred embodiment, an electrochemical cell contains one or more void volumes configured to accept and accommodate migrating gas so as to thereby improve the efficiency of the cell. For example, a cell with an aqueous liquid or gel electrolyte may contain portions of a thin, highly hydrophobic sheet membrane or hollow fibre
5 membrane that is isolated and not in gaseous contact with the environment about it. Such isolated portions of a thin, highly hydrophobic sheet membrane or hollow fibre membrane, may be placed so as to accept and accommodate gas that is slowly but inopportunately generated within the cell during operation. In addition to being isolated from the surroundings, the void volumes within the hydrophobic membranes may also
10 be isolated from each other and, or they may be in gaseous contact with each other.

[0103] The hydrophobic membranes may be located at the edges of the cell outside of the electrical pathway of the cell, or they may be placed in, for example, a lengthwise location, along the electrical pathway, to thereby minimise their footprint for electrical
15 resistance.

[0104] For example, the void volume(s) may accommodate gas that is slowly but inopportunately created within a battery during overcharging, including but not limited to a Ni metal hydride, lead acid, or lithium ion battery, where the uncontrolled formation
20 of independent gas bubbles has the potential to damage the battery or degrade its performance. In such an application, the void volumes may, in effect, replace or partially replace the sacrificial materials that are routinely incorporated to suppress gas formation. The void volume(s) may further act as a "buffer tank" to hold amounts of gases that are formed prior to the reverse, recombination reaction that removes them
25 during discharging.

[0105] In another example, the void volume(s) may accommodate gas formed during the operation of an electrophoretic or electroosmotic cell to thereby improve the operation of the cell. In further non-limiting examples, the void volume(s) may act to
30 halt or minimise the incidence of bubble formation in electrochemical cells with solid-state or gel electrolytes.

[0106] It is to be understood that, even in cases where a void volume is in gaseous isolation from its environment within a liquid media, it may still be capable of accepting substantial quantities of gas. This may arise because a void volume will necessarily and competitively accommodate migrating gas up to the point that the internal gas pressure within the void volume exceeds the so-called “bubble point” of the void volume. At that stage one or more bubbles will form in an uncontrolled manner at the interface between the void volume and the surrounding liquid media. Thus, the fact that a void volume may be in gaseous isolation within a liquid or gel media does not prevent it from accepting and accommodating even substantial quantities of gas. The term “bubble point” is used herein in the context described in the Applicant’s International Patent Publication No. WO2015013764, entitled “*Method and Electrochemical Cell for Managing Electrochemical Reactions*”, which is herein incorporated by reference.

[0107] In another preferred embodiment, the void volume does not merely accept and accommodate migrating gas, but instead, or additionally, forms a gaseous conduit that transports the migrated gas from/to another part of the cell, or into/out of the cell entirely, for example to a holding tank. For example, the void volume may act to allow unwanted gases formed within the electrolyte of the cell to escape from the cell.

[0108] For example, the void volume(s) may transport gas from the electrolyte present between the electrodes, including gas-producing electrodes, to another portion of the cell that lies outside of, or substantially outside of the conduction pathway of the cell, or to the outside of the cell. In other examples, the void volume may act to continuously remove dissolved gases within the liquid- or gel-electrolyte of the cell between the electrodes, to thereby improve the electrical conductivity and hence the electrical efficiency of the cell. That is, the void volume may be used to continuously “de-gas” the electrolyte and vent dissolved gases to the air, so as to thereby improve the electrical conductivity of the electrolyte.

[0109] In other examples, the void volume(s) may act to competitively suppress dissolution of gas within an electrolyte, so as to thereby maximise the electrical conductivity of the electrolyte. In additional examples, the void volume(s) may act to

carry a particular inert gas into the cell, so as to thereby saturate the electrolyte with a gas that is reactively inert and to thereby improve the overall efficiency of the cell.

[0110] In another preferred embodiment, the void volume may be associated with an electrode. That is, the void volume may form the gaseous side of a gas diffusion electrode, where the gaseous side of the electrode lies outside of, or substantially outside of the conduction pathway of the cell between the electrodes, and where the gaseous side of the gas diffusion electrode facilitates the movement of gas into or out of the cell. The gas diffusion electrode may act to transport a gas generated at the electrode out of the cell; alternatively, the gas diffusion electrode may act to transport gas into the cell, from the outside of the cell. Examples of such cells include an 'electrosynthetic' or an 'electro-energy' cell.

[0111] In an embodiment where the electrochemical cell contains at least one gas diffusion electrode, the cell preferably but not exclusively has one or more of the following advantages:

- (1) an ability to conveniently and economically manage a variety of industrial electrochemical processes by deployment of gas diffusion electrodes where only solid-state electrodes had previously been viable or economical;
- (2) an ability to apply higher gas or liquid pressures in electrochemical cells utilizing gas diffusion electrodes than had previously been possible;
- (3) elimination of the need for complex and expensive pressure-equalising equipment in industrial electrochemical cells that currently employ gas diffusion electrodes. The pressure equalising equipment was needed to avoid substantive pressure differentials over the gas and the liquid sides of the gas diffusion electrodes, which would result in leaking of the liquid electrolyte;
- (4) an ability to conveniently and economically facilitate energetically-favourable gas depolarization reactions at electrodes (for example at the counter electrode) in industrial electrochemical cells and/or devices,

where this was attractive from an energy efficiency point of view but had not been previously feasible; and/or

- (5) the possibility of adding a barrier layer or film to a gas diffusion electrode such that it permits transport of the reactant/product gas but excludes water vapour.

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[0112] Preferably but not exclusively, the cell is operated under conditions where the “Electrolyte Factor” (EF; for example in units of: mA.mol / L.s) is increased or maximised to the greatest reasonable extent. The “Electrolyte Factor” (EF; in units of: mA.mol / L.s) reflects the ratio of the conductive capacity of the liquid electrolyte to the extent of gas dissolution and diffusion in the liquid electrolyte. Where multiple gases are involved, the “Electrolyte Factor” (EF; in units of: mA.mol / L.s) reflects the ratio of the conductive capacity of the liquid electrolyte to the sum for all of the gases of the extent of gas dissolution and diffusion in the liquid electrolyte.

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[0113] Accordingly, and preferably but not exclusively, the physical conditions described above are set so as to increase or maximise the conductance of the liquid- or gel-electrolyte between the electrodes in the cell. Furthermore, preferably but not exclusively, the physical conditions described above are set so as to reduce or minimise the dissolution of gas in the liquid- or gel-electrolyte between the electrodes, so as to thereby increase or maximise the electrical conductance of the electrolyte. In the alternative, the physical conditions described above are, preferably but not exclusively, set to reduce or minimise the rate of diffusion of the gases that are dissolved in the liquid- or gel-electrolyte between the electrodes. In a third alternative, the physical conditions described above are, preferably but not exclusively, set to reduce or minimise either the dissolution of gases in the electrolyte, or the rate of diffusion of the gases in the electrolyte, or a suitable combination thereof, so as to increase or maximise the efficiency of the cell in operation and/or from an energy or electrical efficiency viewpoint.

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[0114] Thus the one or more void volumes, e.g. a pre-existing bubble, gas region or gas pathway, either naturally occurring or man-made, in different examples, can be positioned:

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- 5 (i) outside of the electrical conduction pathway between electrodes,
(ii) substantially outside of the electrical conduction pathway between electrodes,
(iii) partially outside of the electrical conduction pathway between electrodes,
(iv) peripheral to or adjacent to the electrical conduction pathway between electrodes,
(v) between the electrodes and within the electrical conduction pathway, but having a small cross-sectional area relative to the electrical conduction pathway between electrodes,
10 (vi) between the electrodes and parallel to the electrical conduction pathway, so as to have a small cross-sectional area relative to the electrical conduction pathway between electrodes,
(vii) between the electrodes and perpendicular to one or both of the electrodes, so as to have a small cross-sectional area relative to the electrical conduction pathway between electrodes, and/or
15 (viii) within, partially within, adjacent to or next to a liquid electrolyte, or gel electrolyte of the cell.
- 20 [0115] Preferably but not exclusively, the cell can be operated under conditions where the Crossover (CO; for example in %), is reduced or minimized to the greatest reasonable extent. The Crossover (CO; in %) is the percentage of gases that cross from one electrode to the other due to gas migration in the liquid electrolyte.
- 25 [0116] In example embodiments, the Crossover (CO) is preferably less than or equal to 40 %. In example embodiments, the Crossover (CO) is less than or equal to 30 %, less than or equal to 20 %, less than or equal to 15 %, less than or equal to 12 %, less than or equal to 10 %, less than or equal to 8 %, less than or equal to 5 %, less than or equal to 4 %, less than or equal to 3 %, less than or equal to 2 %, less than or equal to 1 %, or
30 less than or equal to 0.5 %. In each case, the Crossover (CO) is greater than or equal to 0 %. In another example, the Crossover (CO) is equal to or about 0 %.

High Pressure Operation

[0117] In example embodiments, methods for facilitating the operation of electrochemical cells at high pressures, are described in the Applicant's concurrent
5 International Patent Application for "High pressure electrochemical cell", filed on 14 December 2016, which is incorporated herein by reference.

[0118] In particular example embodiments, the inventors have discovered that the operation of an electrochemical cell, under the conditions described herein, can allow
10 for cells that are capable of operating at higher pressures than are viable in many conventional systems. Additionally, the higher pressures are accompanied by greater energy efficiency and/or higher current densities. That is, in particular example embodiments, the inventors have discovered that the advantages of modes of operating the example electrochemical cells described herein, relative to comparable,
15 conventional cells, are so unexpectedly amplified as to allow for economically-viable operation under hitherto unavailable or unviable conditions of pressure.

[0119] Increases in the applied pressure in electrochemical cells of example embodiments should not degrade the purity of the one or more gases collected at the
20 anode and/or cathode, at least not to near the extent observed in conventional cells. Moreover, when operated in the described way, such cells are substantially more electrically and energy efficient than comparable conventional cells. Increases in current density at high pressure can also have the effect of progressively improving, and not degrading, the gas purity as is the case for conventional cells. This can be
25 accompanied by high energy efficiency and/or high current densities. This realisation has important practical utility since it can yield new industrial electro-synthetic and electro-energy processes that operate under hitherto unavailable or unviable conditions of pressure and/or current density.

30 [0120] It should be noted that "pressure" as used herein (including reference to "high pressure"), unless otherwise stated, refers to the "gas pressure" (e.g. a gaseous product(s) pressure), which is necessarily similar or close to, but somewhat below the "electrolyte pressure" (e.g. a liquid electrolyte pressure). The "electrolyte pressure"

should not be more than the “gas pressure” plus the “wetting pressure of a membrane” (otherwise the membrane will leak/flood). In general, by way of example, the “gas pressure” is typically set to about 0.5 bar to about 1.5 bar below the “electrolyte pressure”.

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[0121] In example embodiments, high pressure (i.e. the pressure) is preferably greater than or equal to 10 bar. In alternative example embodiments, high pressure is preferably greater than or equal to 20 bar, greater than or equal to 30 bar, greater than or equal to 40 bar, greater than or equal to 50 bar, greater than or equal to 60 bar, greater than or equal to 70 bar, greater than or equal to 80 bar, greater than or equal to 90 bar, greater than or equal to 100 bar, greater than or equal to 200 bar, greater than or equal to 300 bar, greater than or equal to 400 bar, or greater than or equal to 500 bar.

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[0122] For example, the inventors have remarkably discovered that the problem of (i) gas crossover through the separator and the problem of (ii) gas pressure equalisation across the separator in an alkaline electrolyzer under high pressure conditions, as described in WO2013/066331 and on pages 160-161 in the book “Hydrogen Production by Electrolysis”, by A. Godula-Jopek (Wiley-VCH, 2015), can be eliminated or drastically curtailed by using appropriate gas diffusion electrodes at the anode and cathode and then removing the separator entirely.

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[0123] Provided that the gas diffusion electrodes, have a suitably high wetting pressure and the pressure differential of the liquid over the gas side of the electrodes is never allowed to exceed that wetting pressure, then it is possible to find physical conditions under which gas crossover is minimal and certainly far less than in a conventional electrochemical cell. As a result, it becomes possible to produce gases of high purity at high pressures.

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[0124] Removing the diaphragm, separator or ion exchange membrane also avoids the difficulties involved in equalising the pressure of the catholyte and anolyte chambers as observed in, for example, the electrolyzer developed by Avalence LLC described in WO2013/066331 and on pages 160-161 in the book “Hydrogen Production by Electrolysis”, by A. Godula-Jopek (Wiley-VCH, 2015). When the separator is removed, the catholyte and anolyte chambers become one, so that no pressure

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differential can then exist between the cathode and anode, at least from the pressure applied to the electrolyte. In concert with avoiding bubble formation, removal of the separator further eliminates crossover deriving from gas bubbles occupying the pores of the separator as observed in, for example, the aforementioned electrolyzer developed by
5 Avalence LLC as described in WO2013/066331 and on pages 160-161 in the book “Hydrogen Production by Electrolysis”, by A. Godula-Jopek (Wiley-VCH, 2015).

[0125] The absence or substantial absence of bubbles in the liquid electrolyte further means that increasing current densities do not create an increasing electrical resistance
10 and diminished energy efficiency arising from the “bubble overpotential”, “bubble-curtain” and “voidage” effects. For this reason, there is also a reduced requirement to rapidly pump electrolyte around the cell. Instead, higher current densities (at high pressures) have a beneficial effect, which involves mitigating and diminishing the relative amount of the gas crossover that occurs due to the migration of dissolved gases
15 in the liquid electrolyte between the electrodes. The rate of such migration may be much smaller than that of bubble migration through a separator. It is also fixed by the physical conditions employed, including temperature, the concentration of salts in the liquid electrolyte, the extent of separation of the electrodes, the pressure applied on the liquid electrolyte and so forth. Since its rate is fixed, increasing the rate of overall gas
20 generation by increasing the current density (under conditions of high pressure), acts to decrease the relative contribution of such gas crossover to the overall rate of gas production. In so doing, the impurities in the product gases created by gas crossover of this type become smaller, including vanishingly small, as the overall current density increases. That is, increases in current density at high pressure increase the purity of
25 the gases generated and this occurs with high overall electrical efficiency.

[0126] These properties stand in stark contrast to the statement in the presentation for project PD117 in the 2015 Annual Merit Review Proceedings (Hydrogen Production and Delivery) of the US Department of Energy, to the effect that it is at present “*Not*
30 *possible to have high efficiency at high pressures*”. Moreover, these unexpected properties overcome the fundamental impediments in high pressure alkaline electrolyzers, as illustrated in the electrolyzer developed by Avalence LLC described in WO2013/066331 and on pages 160-161 in the book “Hydrogen Production by

Electrolysis”, by A. Godula-Jopek (Wiley-VCH, 2015), operation of which is limited both in the current density (at high pressure) that can be efficiently applied and the fact that increases in pressure lead to increasingly impure gases (thereby, ultimately, limiting the maximum applied pressure).

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[0127] As a result of these properties, the example electrochemical cells as described herein and in the Applicant’s concurrent International Patent Applications entitled “Electrochemical cell and components thereof capable of operating at high current density” and “Electrochemical cell and components thereof capable of operating at high voltage”, filed on 14 December 2016, which are incorporated herein by reference, can, unexpectedly, be used to generate high pressure gases of high purity at, optionally, a high current density and with, optionally, high electrical and energy efficiency without the need for a gas compressor. Similar principles apply to the reverse situation, namely fuel cells of the abovementioned type, which may utilize high pressure gases of high purity, at a high current density, to achieve high electrical and energy efficiency.

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[0128] Accordingly, in one aspect, embodiments provide for an electrochemical cell that generates one or more high purity gases at high pressure from a liquid electrolyte, without a gas compressor. Preferably, the cell operates with high electrical and energy efficiency.

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[0129] Preferably, bubbles of the gas are not formed or produced, or are substantially not formed or produced at the gas-producing electrode.

[0130] Also preferably, there is no diaphragm, separator or ion exchange membrane positioned between the gas-producing electrode and the counter electrode, i.e. between the anode and the cathode. In another example, the method includes selecting an Inter-electrode Distance (ID) between the electrodes and/or selecting a Current Density (CD) so that a Crossover (CO) for the electrochemical cell is less than or equal to 40 %. Optionally, the Crossover (CO) is equal to or about 0 %. In one example, one or more void volumes are located at or adjacent to the gas-producing electrode. An example method comprises operating the electrochemical cell at a current density greater than or equal to 50 mA/cm² and at a pressure greater than or equal to 10 bar.

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[0131] In example embodiments, high purity of a gas is preferably greater than or equal to 90%. In alternative example embodiments, high purity of a gas is preferably greater than or equal to 95%, greater than or equal to 97%, greater than or equal to 99%, greater than or equal to 99.5%, greater than or equal to 99.9%, greater than or equal to 99.99%,
5 greater than or equal to 99.999%, greater than or equal to 99.9999%, or greater than or equal to 99.99999%. In another example, a produced gas has a purity equal to or about 100%.

[0132] In example embodiments, high pressure is preferably greater than or equal to 10
10 bar. In alternative example embodiments, high pressure is preferably greater than or equal to 20 bar, greater than or equal to 30 bar, greater than or equal to 40 bar, greater than or equal to 50 bar, greater than or equal to 60 bar, greater than or equal to 70 bar, greater than or equal to 80 bar, greater than or equal to 90 bar, greater than or equal to 100 bar, greater than or equal to 200 bar, greater than or equal to 300 bar, greater than
15 or equal to 400 bar, or greater than or equal to 500 bar.

[0133] In another aspect, the electrochemical cell generates high purity gases at high pressure from a liquid electrolyte at high current density and without a gas compressor.

20 [0134] In another example, the electrochemical cell generates high purity gases at high pressure from a liquid electrolyte without a gas compressor, where the electrochemical cell combines at least one or both of a gas diffusion anode and a gas diffusion cathode, both of which have relatively high wetting pressures.

25 [0135] In example embodiments, high wetting pressure is preferably greater than or equal to 0.2 bar. In alternative example embodiments, high wetting pressure is preferably greater than or equal to 0.4 bar, greater than or equal to 0.6 bar, greater than or equal to 0.8 bar, greater than or equal to 1 bar, greater than or equal to 1.5 bar, greater than or equal to 2 bar, greater than or equal to 2.5 bar, greater than or equal to 3
30 bar, greater than or equal to 4 bar, or greater than or equal to 5 bar.

[0136] In example embodiments, only a lessened or minor requirement to pump electrolyte around the cell is necessary, the electrolyte replacement rate is preferably

less than 1 replacement of the electrolyte in the cell volume every 1 hour. In alternative example embodiments, the electrolyte replacement rate is preferably less than 1 replacement of the electrolyte in the cell volume every 45 minutes, less than 1 replacement of the electrolyte in the cell volume every 30 minutes, less than 1 replacement of the electrolyte in the cell volume every 15 minutes, less than 1 replacement of the electrolyte in the cell volume every 10 minutes, less than 1 replacement of the electrolyte in the cell volume every 5 minutes, less than 1 replacement of the electrolyte in the cell volume every 1 minute, less than 1 replacement of the electrolyte in the cell volume every 30 seconds, less than 1 replacement of the electrolyte in the cell volume every 5 seconds, or less than 1 replacement of the electrolyte in the cell volume every 1 second.

[0137] In a further example aspect, there is provided electro-synthetic or electro-energy cells, such as an electrochemical cell or a fuel cell, with one or more gas diffusion electrodes that are bubble-free or substantially bubble-free in operation, wherein the cell is operated at high pressure and/or high current density. Similar principles apply to the reverse situation, namely: cells of the abovementioned type can utilize high purity gases at high pressure (obtained with or without use of a compressor), at, optionally, a high current density, to thereby, optionally, achieve high electrical and energy efficiency.

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[0138] These examples provide for:

- (1) An electrochemical cell that does not contain an ion-permeable diaphragm between the anode and the cathode of the cell, and that generates high purity gases, or one or more pure gases, at high pressure from a liquid or gel electrolyte, without need for a gas compressor.
- (2) An electrochemical cell that does not contain an ion-permeable diaphragm between the anode and the cathode of the cell, and that operates in a bubble-free manner or substantially bubble-free manner, to generate high purity gases, or one or more pure gases, at high pressure from a liquid or gel electrolyte, without need for a gas compressor.
- (3) An electrochemical cell that does not contain an ion-permeable diaphragm between the anode and the cathode of the cell, and that operates in a bubble-free or substantially bubble-free manner, to generate

high purity gases, or one or more pure gases, at high pressure from a liquid or gel electrolyte, without need for a gas compressor, where the cell operates:

- i. with high current density and/or high energy efficiency; and/or
- 5 ii. where increases in the current density yield increases in the purity of the gases produced.

Operation Involving Sudden and Large, Intermittent and/or Fluctuating Currents

10 [0139] In example embodiments, electrochemical cells and/or methods for handling rapid increases in current, or equivalently current density, in electrochemical cells, including under conditions of highly intermittent and/or fluctuating current supply, such as may be afforded by a renewable energy source, like wind generators, solar panels or ocean wave/tidal generators, are described.

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[0140] Many known gas generating liquid-filled electrochemical cells, like conventional alkaline electrolyzers, cannot handle sudden and large increases in current as may occur when they are directly connected to highly intermittent current supplies, such as may be afforded by renewable energy sources like wind generators, solar panels
20 or ocean wave/tidal generators. In the case of a very rapid rise in current, a large amount of gas may be produced very quickly in such cells, creating a potential pressure burst hazard and also potentially forcing the liquid electrolyte out of the cell, thereby damaging the cell either mechanically, or electrochemically, or both.

25 [0141] Where porous electrodes have been used, it may also be imperative to avoid sudden, large-scale gas evolution in the pores since the formation of bubbles in this way can mechanically damage the catalyst, causing crumbling or erosion of the catalyst particles. There are various other ways in which a cell may be damaged by a sudden current surge.

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[0142] Various patents teach methods and procedures by which to instantly or progressively cut liquid-filled cells off from an electrical supply when its current surges too strongly. For example, US20140120388 teaches of a cut-off switch for a battery

during recharging where the activation of the cut-off switch is linked to the pressure of any gas that may be produced. US20120181992 teaches of a cut-off switch that is linked to the voltage of a battery connected to an intermittent source of energy. US20110156633 teaches of a solar power system that modulates the voltage of the incoming, intermittent current, in order to avoid damage. Conventional alkaline electrolyzers must typically be operated at current densities of around 300 mA/cm² with surges in current or current density limited to no more than ca. 20-30% of that value.

[0143] By contrast, in particular examples the inventors have discovered that the example electrochemical cells as described herein, which operate most economically at low current densities, are unexpectedly able to be operated under conditions of remarkably large and sudden surges or variations in current, with no or little noticeable degradation in subsequent performance.

[0144] Experiments have shown that the example electrochemical cells as described herein can be operated under unexpected conditions or ranges to routinely handle current surges of at least 25-fold over their normal operating currents, for example delivered over several milliseconds. Moreover, testing has revealed that the electrochemical cells can handle surges of such scale repeatedly, without noticeable degradation in electrochemical performance, at intervals of a few seconds, applied continuously and without break, over periods exceeding six months. To the best of the inventors' knowledge, no other cell types and most especially no other liquid-containing cells, are capable of such performance.

[0145] The origin of this remarkable capability appears to lie in it being energetically more favourable for newly formed or dissolved gas within a liquid to join a large, pre-existing bubble than it is for the gas to form a new bubble. Moreover, the concentration of dissolved gas within a liquid electrolyte is also minimised and held below supersaturation levels, about a pre-formed bubble since the bubble provides an additional interface through which excess gaseous molecules may quickly and easily escape the liquid phase. Thus, it is, effectively, impossible for a liquid electrolyte to become supersaturated near to an existing bubble, since the bubble interface provides a ready and favourable route for the excess gas to escape the liquid phase.

[0146] Accordingly, if an “artificial bubble”, such as the gas side or region of a gas diffusion electrode is present near to the point of formation of a gas in a liquid-containing cell, then the newly formed gas is strongly favoured to join that “artificial bubble” rather than to form a new bubble or dissolve in a supersaturated way within the liquid. Moreover, if that “artificial bubble” has a substantial volume and a large gas-liquid interface, then it can accommodate and absorb even very large quantities of a gas that may be formed extremely suddenly in the liquid phase. In other words, the “artificial bubble”, represented by the gas side of a gas diffusion electrode, may act as a buffer that rapidly assimilates and removes even substantial quantities of gas formed very quickly within the liquid phase. In this way, the damage that may be caused by sudden, large-scale bubble formation may be eliminated in its entirety, or, at least, mitigated to a substantial extent.

[0147] Furthermore, because the “artificial bubble”, represented by the gas side of a gas diffusion electrode, lies outside of the electrical conduction pathway through the liquid electrolyte, the sudden formation of large quantities of gas need not affect in any substantial way, the electrical resistance of the liquid electrolyte. That is, not only is the potentially damaging effect of sudden bubble formation mitigated, but the electrical resistance and hence the electrical and energy efficiency of the cell, may also be substantially unaffected. In other words, the cell remains capable of operating with amplified energy efficiency relative to conventional cells, during sudden and large-scale surges in current.

[0148] Referring to Figure 3, there is illustrated a method 300 for operating an electrochemical cell. The electrochemical cell comprises one or more void volumes, a gas-producing electrode, and a counter electrode. The gas-producing electrode and the counter electrode being separated by an electrolyte. The method 300 includes, at step 310, supplying an intermittent or fluctuating current to at least the gas-producing electrode. At step 320, a gas is produced at the gas-producing electrode as a result of an electrochemical reaction. At step 330, the gas is received by the one or more void volumes.

[0149] These realisations provide for:

- 5 (1) A liquid- or gel-containing electrochemical cell that is capable of accommodating or receiving large and sudden increases and/or fluctuations in an applied current without experiencing substantive damage, the cell including:
- 10 i. one or more void volumes positioned or located outside of, or substantially outside of, or partially outside of, or on the periphery of, or within but only providing a small cross-section of, the electrical conduction pathway through the liquid or gel electrolyte; and
- ii. current collectors and/or electrodes;
- where
- 15 iii. the one or more void volumes are capable of accommodating the gases generated during large and sudden increases and/or fluctuations in an applied or supplied current; and
- iv. the current collectors and/or electrodes in the cell are capable of accommodating or receiving large and sudden increases and/or fluctuations in an applied or supplied current.
- 20 (2) A method for fabricating a liquid- or gel-containing cell that is capable of accommodating or receiving large and sudden increases and/or fluctuations in an applied or supplied current without experiencing substantive damage, the method involving
- 25 i. positioning or locating one or more void volumes within, adjacent to or near to the liquid or gel electrolyte, but outside of, or substantially outside of, or partially outside of, or on the periphery of, or within but only providing a small cross-section of, the electrical conduction pathway through the liquid or gel electrolyte; and
- 30 ii. locating current collectors and/or electrodes within the cell;
- where

- iii. the one or more void volumes are capable of accommodating the gases generated during such surges; and
- iv. the current collectors and/or electrodes in the cell are capable of accommodating the currents involved in such surges.

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[0150] In an example embodiment, the one or more void volumes, as previously discussed herein, do not merely accept and accommodate migrating gas, but instead, or additionally, form a gaseous conduit that transports the migrated gas from/to another part of the cell, or into/out of the cell entirely, for example to a holding tank. For
10 example, the void volume(s) may act to allow unwanted gases formed within the electrolyte of the cell to escape from the cell.

[0151] For example, the one or more void volumes can act to allow gases formed rapidly within the electrolyte of the electrochemical cell to escape from the cell into an
15 external holding tank, or to be vented to the atmosphere. In example embodiments, the one or more void volumes can transport gas that is formed rapidly and suddenly, from the electrolyte present between the electrodes to another portion of the cell that lies outside of, or substantially outside of the conduction pathway of the cell, or to the outside of the cell.

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[0152] In such embodiments, preferably but not exclusively, the total void volume, including the conduit and the holding tank, or the outside atmosphere, is large or very large relative to the gas volumes that may be created by rapid and sudden surges in the electrical current. That is, preferably, but not exclusively, the total void volume is such
25 as to provide a capacity to readily absorb large quantities of gas or gases that may be formed rapidly and suddenly within the electrochemical cell.

[0153] For example, the one or more void volumes can be positioned so as to provide a pathway for gas that is rapidly and suddenly created within the electrolyte between the
30 electrodes in a battery during overcharging, including but not limited to a Ni metal hydride, lead acid, or lithium ion battery, where the uncontrolled formation of independent gas bubbles has the potential to damage the battery or degrade its performance. In such an application, the one or more void volumes can, in effect,

replace or partially replace the sacrificial materials that are routinely incorporated to suppress gas formation. The void volume(s) can transport the gas to a separate volume within the cell that acts as a “buffer tank” to hold amounts of gases that are formed prior to the reverse, recombination reaction that removes them during discharging.

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[0154] In another example, the void volume(s) can transport gas formed rapidly and suddenly, from the electrolyte between the electrodes to another portion of the cell that lies outside of the conduction pathway of the cell, or to the outside of the cell, during the operation of an electrophoretic or electroosmotic cell to thereby improve the operation of the cell. In further non-limiting examples, void volume(s) of this type can act to halt or minimise the incidence of bubble formation in electrochemical cells with solid-state or gel electrolytes.

[0155] In other examples, the one or more void volumes can act to continuously remove dissolved gases that are rapidly and suddenly formed within the liquid-electrolyte or gel-electrolyte of the electrochemical cell between the electrodes, to thereby maintain and/or improve the electrical conductivity and hence maintain and/or improve the electrical efficiency of the cell. That is, the one or more void volumes can be used to continuously “de-gas” the electrolyte and vent dissolved gas or gases that are formed rapidly and suddenly, to a holding tank, or outside to the air, so as to thereby maintain and/or improve the electrical conductivity of the electrolyte.

[0156] In example embodiments, the electrochemical cell provides a means for accommodating sudden, large increases in the current (or current density). In example embodiments, sudden, large increases in the current refer to preferably more than double the current. In alternative example embodiments, sudden, large-scale increases in the current refers to preferably more than triple the current, more than four-fold the current, more than five-fold the current, more than six-fold the current, more than eight-fold the current, more than ten-fold the current, more than twelve-fold the current, more than fifteen-fold the current, more than twenty-fold the current, or more than twenty-five-fold the current.

[0157] The large increase in the current can be sudden and occur over a duration of less than a millisecond, about a millisecond, less than 10 milliseconds, less than 100

milliseconds, less than a second, less than a few seconds, less than 10 seconds, or less than a minute.

[0158] In further preferred embodiments, the current collectors, catalysts, and/or electrodes in the cell are capable of operating at high current densities, so as to thereby accommodate large and sudden increases and/or fluctuations in the applied/supplied current.

[0159] In further preferred embodiments, the current collectors, catalysts, and/or electrodes in the cell are capable of operating at high pressures, so as to thereby accommodate large and sudden increases and/or fluctuations in the gases formed.

[0160] In further preferred embodiments, the current collectors, catalysts, and/or electrodes in the cell are capable of operating at high energy efficiencies, so as to thereby accommodate large and sudden increases and/or fluctuations in the currents applied and gases generated.

[0161] In a further example aspect, there is provided electro-synthetic or electro-energy cells, such as an electrochemical cell or a battery, containing a liquid-electrolyte or a gel-electrolyte with one or more gas diffusion electrodes, which are capable of accommodating large quantities of gases that may be formed rapidly and suddenly within the cell due to fluctuations and/or intermittency in the current.

[0162] In a further example aspect, there is provided an electro-synthetic or electro-energy cell, such as an electrochemical cell or a battery, containing a liquid- electrolyte or gel-electrolyte with one or more gas diffusion electrodes, which are capable of accommodating or receiving large fluctuations and/or intermittency in the current that result in the rapid and sudden generation of substantial quantities of gases within the cell.

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[0163] In another example aspect, there is provided an electro-synthetic or electro-energy cell, comprising a liquid-electrolyte or gel-electrolyte and at least one gas diffusion electrode; the one or more gas diffusion electrodes being bubble-free or

substantially bubble-free, wherein in use the cell is operated with large fluctuations and/or intermittency in the current, resulting in the rapid and sudden generation of substantial quantities of gases.

5 [0164] In another aspect, there is provided a gas-liquid electrochemical cell capable of directly harnessing an intermittent energy source, such as a solar-powered or a wind-powered or an ocean wave/tidal powered renewable energy source, without notable modulation or conditioning of the current (which can be direct current, e.g. from a solar panel, or alternating current, e.g. from a wind turbine). For example, instead of
10 converting the electrical current output of a solar-generator or a wind-generator or an ocean wave/tidal-generator into alternating current of near-uniform intensity, the raw output of intermittent current produced by such a generator can be directly harnessed by an example electrochemical cell as described herein. This eliminates a number of energy losses, allowing for more efficient use of renewable energy sources, such as
15 solar-generators, wind-generators and ocean wave/tidal-generators.

[0165] In example embodiments, intermittent power of this type can be practically employed in the electrochemical manufacture of a host of standard industrial products, including, but not exclusively: (a) chlorine, (b) hydrogen peroxide, (c) ozone, (d)
20 caustic (with or without chlorine), (e) potassium permanganate, (f) chlorate, (g) perchlorate, (h) fluorine, (i) bromine, (j) persulfate, (k) fuels from CO₂, (l) CO₂ from methane, and others.

[0166] In alternative example embodiments, electrochemical cells involving
25 electrochemical processes unique to particular industries can be powered by intermittent renewable energy sources, including but not restricted to:

- (i) electrometallurgical applications, such as metal electrowinning;
- (ii) pulp and paper industry applications, such as: (a) "*black liquor*" electrolysis, (b) "*Tall Oil recovery*" and (c) chloride removal electrolysis.

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[0167] In a further aspect, example electrochemical cells can be used to generate electrochemical energy, where the fuel for the energy may only be supplied intermittently, sporadically, or in a highly fluctuating manner. For example, fuel cell

and related device applications, such as hydrogen-oxygen fuel cells, including but not limited to alkaline fuel cells, where the fuel (in the form of the gases oxygen and hydrogen) is supplied in a fluctuating, intermittent or highly variable manner, can be realised.

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[0168] In a still further aspect, example electrochemical cells can be used to facilitate improved recycling or disposal of unwanted materials, relative to what would otherwise have been the case, using intermittent energy sources, like solar-powered or wind-powered or ocean wave/tidal-powered renewable electricity and/or intermittently available feedstocks, such as air oxygen.

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[0169] In another aspect, example electrochemical cells can be used to facilitate improved management of electrical grids that receive notable inputs from intermittent energy source, such as solar-powered.

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High Electrical and/or Energy Efficiency Operation

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[0170] In example embodiments, methods for operating cells at high electrical and energy efficiencies, are described in the Applicant's concurrent International Patent Application entitled "Method and system for efficiently operating electrochemical cells", filed on 14 December 2016, which is incorporated herein by reference.

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[0171] Example methods for operating cells at high electrical and energy efficiencies may occur when an endothermic electrochemical reaction is facilitated. In such applications, the cells can act to minimise or, at least, noticeably decrease the intrinsic energy inefficiencies involved in electrochemical cells that facilitate liquid-gas reactions. For example, the energy sapping influence that bubbles may have in such cases, may be substantially mitigated.

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[0172] In particular example embodiments, the inventors have further recognised that, for such endothermic electrochemical reactions, there may be at least one catalyst available that is capable of sustainably catalyzing the reaction at cell voltages below or near to the so-called "thermoneutral voltage", which represents the maximum possible

energy efficiency with which the cell can operate. In order to properly realise the potential energy efficiencies, it may be necessary to employ cells of the present embodiments, which provide a minimisation or, at least, a noticeable reduction in the intrinsic inefficiencies that may otherwise have been present.

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[0173] In example embodiments, the electrical efficiency is defined as the ratio of the total energy put into the cell relative to the total energy incorporated in the products generated by the cell over a particular time period. In example embodiments, high electrical and energy efficiency is preferably greater than or equal to 70%. In
10 alternative example embodiments, high electrical and energy efficiency is preferably greater than or equal to 75%, greater than or equal to 80%, greater than or equal to 85%, greater than or equal to 87%, greater than or equal to 90%, greater than or equal to 93%, greater than or equal to 95%, greater than or equal to 97%, greater than or equal to 99%, or greater than or equal to 99.9%.

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[0174] New methods of operation of the example electrochemical cells at or near ambient (e.g. room) temperature as described herein, are predicated on the fact that the cells may be operated economically-viably at low current densities. They may also be utilized to facilitate reactions which are endothermic in nature; that is, reactions which
20 absorb heat. This is significant since, for reactions of that type, there may be catalysts available that catalyze the reaction at cell voltages below the so-called "thermoneutral" voltage at or near ambient (e.g. room) temperature but they can only do so at low current densities.

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[0175] Thus, the inventors have understood that operating a suitable catalyst at operational voltages below, at, about or near to the thermoneutral voltage, at or near to ambient temperatures, where they produce only low current densities, within cells that operate viably at low current densities, offers a useful approach to the development of energy efficient liquid-gas electrochemical cells.

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[0176] The inventors have further realised that at a fixed current density, the operational voltage of such a cell may decline with an increase in temperature. That is, higher current densities at, about or near to the thermoneutral voltage may be achieved for a suitable catalyst by increasing the temperature of the cell. Provided the cell is

capable of withstanding the higher temperatures without damage or impairment, it is possible to operate cells at, about, or near to the thermoneutral voltage with higher current densities at higher temperatures.

5 [0177] Thus, the inventors have understood that operating a suitable catalyst at operational voltages below, at, about or near to the thermoneutral voltage at higher temperatures, where they produce higher current densities, within cells that capable of withstanding the higher temperatures without damage or impairment, offers a useful approach to the development of energy efficient liquid-gas electrochemical cells.

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[0178] The inventors have, additionally, understood that another useful approach to thermal management in such cells, known as “thermal self-regulation”, involves allowing the operational temperature of the cell to vary in accordance with the thermal parameters and not be fixed. That is, a useful approach to thermal management
15 involves allowing the cell to find its own optimum operating temperature in a process of “thermal self-regulation”. Optionally, this may be done with the cell wrapped in thermal insulation. This approach involves applying a particular current density as required (in the presence of suitable catalysts). If, at the temperature of the cell, the applied current density creates a higher voltage in the cell than the thermoneutral
20 voltage, then the cell will progressively heat itself up. As the cell heats itself up, the cell voltage will typically decline. At the applied, fixed, current density, the cell will continue heating itself up until such time as the cell voltage has declined to be at, about, or near to the thermoneutral voltage (depending on the quality of the thermal insulation). At that point, the temperature of the cell will stabilize and cease increasing.
25 During the entire process the cell would be operating at as close to 100% energy efficiency as the thermal insulation will allow. The reverse of the above will occur (causing a decrease in the operating temperature of the cell) if the current density that is applied causes the cell voltage to decline.

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[0179] The thermoneutral voltage is defined as that cell voltage at which the heat generated by the catalyst and associated conductors is equal to the heat consumed by the reaction. If an endothermic electrochemical reaction is carried out at the thermoneutral voltage, then the energy and electrical efficiency of the conversion of

reactants into products is, by definition, 100%, since all of the energy that is put into the cell is necessarily converted into energy within the products of the reaction. That is, the total electrical and heat energy input into the cell is matched with the total energy present in the products of the reaction with no excess input energy radiated to the surroundings. However, if the reaction is carried out above the thermoneutral voltage, then excess energy is generated, usually in the form of heat. If the reaction is carried out below the thermoneutral voltage, then energy, usually heat, needs to be added in order to avoid self-cooling by the system.

[0180] In particular example embodiments, the inventors have realised that example electrochemical cells as described herein can be operated at, below, or near to the thermoneutral potential in an economically-viable way, for example so as to avoid the need for extensive and energy-sapping electrical cooling systems. This realisation has important and far-reaching implications for the heat management and energy efficiency of such cells. With sufficiently powerful catalysts and/or suitably high temperatures, example electrochemical cells of the type described in Applicant's concurrent International Patent Applications entitled "Electrochemical cell and components thereof capable of operating at high current density" and "Electrochemical cell and components thereof capable of operating at high voltage", filed on 14 December 2016, which are incorporated herein by reference, can be operated at, below, or near to the thermoneutral potential in an economically-viable way.

[0181] In particular example embodiments, the inventors have produced suitable example catalysts, which facilitate electrocatalytic water electrolysis. The catalyst(s) is applied to at least one of, or both of, the electrodes to facilitate the endothermic electrochemical reaction at the operational voltage of the electrochemical cell. In preferred but non-limiting examples, the catalyst contains one or more of the following catalytic materials: (i) Precious metals, either free or supported, including but not limited to Pt black, Pt supported on carbon materials (e.g. Pt on carbon black), Pt/Pd on carbon materials (e.g. Pt/Pd on carbon black), IrO₂, and RuO₂; (ii) Nickel, including but not limited to: (a) nanoparticulate nickels, (b) sponge nickels (e.g. Raney nickel), and (c) nickel foams; (iii) Nickel alloys, including but not limited to, NiMo, NiFe, NiAl, NiCo, NiCoMo; (iv) Nickel oxides, oxyhydroxides, hydroxides, and combinations

thereof, without limitation; (v) Spinel, including but not limited to NiCo_2O_4 , Co_3O_4 , and LiCo_2O_4 ; (vi) Perovskites, including but not limited to $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$, and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$; (vii) Iron, as well as iron compounds, including but not limited to nanoparticulate iron powders and the like; (viii) 5 Molybdenum compounds, including but not limited to MoS_2 ; (ix) Cobalt, as well as cobalt compounds, including but not limited to nanoparticulate cobalt powders and the like; and (x) Manganese, as well as manganese compounds, including but not limited to nanoparticulate manganese powders and the like.

10 [0182] In another example, the catalyst/s comprises one or more of the above catalytic materials mixed in with PTFE (e.g. in a 5% dispersion in alcohol from Sigma-Aldrich), creating a slurry. The slurry is preferably, but not exclusively, coated, for example knife-coated, onto the electrode(s) and conductor(s) in a layer or coating. In one particular example, after drying, the catalyst contains about 40% by weight PTFE, 15 about 60% by weight of the catalytic materials. Optionally, carbon black may also be added to the slurry.

[0183] The above percentages of component materials in the catalyst can be varied and the catalyst can remain functional. For example, suitable ranges for the catalyst, when 20 dry, are:

about 5% to about 95% by weight of PTFE, and
about 5% to about 95% by weight of the catalytic materials.

[0184] In another example, suitable ranges for the catalyst, when dry, are: 25 about 5% to about 90% by weight of PTFE,
about 5% to about 90% by weight of uncoated carbon black, and
about 5% to about 90% by weight of the catalytic materials.

[0185] In another example, there is no ion exchange membrane positioned between the 30 electrodes. In another example, there is no diaphragm positioned between the electrodes. In another example, the electrolyte is a liquid electrolyte or a gel electrolyte. In another example, bubbles of the produced gas, or at least one gas, are not, or are substantially not produced or formed at either of the electrodes.

[0186] Conventional cells that can only operate economically above the thermoneutral potential, will necessarily develop excess heat which has to be removed by a suitable cooling system during operation. Cooling systems, such as chillers, are typically expensive and energy inefficient. Thus, not only does such a conventional cell operate at a voltage that creates and wastes excess heat, but further energy must then be expended to remove that excess heat. The resulting multiplier effect will typically have the effect of dramatically diminishing the overall energy efficiency of the cell during routine operation. For example, small-scale water electrolyzers that generate 0.5-10 kg/day of hydrogen during routine operation, typically consume 75-90 kWh per kilogram of hydrogen produced. However, one kilogram of hydrogen, in fact, only requires 39 kWh of energy to manufacture. The difference is largely due to the waste heat that is generated and the need for an energy inefficient chiller to remove the waste heat.

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[0187] By contrast, an electrochemical cell that operates at, below, or near to the thermoneutral potential does not create substantial excess heat that needs to be removed. If an electrochemical cell can be operated near the thermoneutral potential, then there may be so little excess heat generated that it is easily lost to the surroundings without any need for a formal or dedicated cooling system. Alternatively, the excess heat can be used to maintain a particular operating temperature that is higher than ambient temperature. If an electrochemical cell can be operated at the thermoneutral potential, there is no heat exchanged with the surroundings at all. If an electrochemical cell can be operated below the thermoneutral potential, then heat must be applied to the cell/system in order to maintain the cell/system temperature and prevent it from cooling. However, in such an unexpected mode of operation, the inventors have realised that such required heat can be, relatively easily, efficiently and quickly, produced using electricity; for example, by resistive heating. Moreover, it becomes possible to apply only so much heat as is needed to maintain the cell temperature, thereby ensuring that the cell wastes no energy and operates at as close to 100% efficiency as is possible.

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[0188] By these means, heat management of an endothermic reaction in an electrochemical cell can become a drastically simpler and more efficient matter than is possible at present. In effect, the common and usually problematic phenomenon of heating in electrochemical cells can be turned into an advantage in cells that operate in an economically-viable way below the thermoneutral potential. That is, it may be utilized to ensure the cell is operating at the maximum possible efficiency. Such an option is not available to conventional cells that must operate at high current densities in order to be economically viable and/or that may be irretrievably damaged or impaired at high operating temperatures.

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[0189] For example, water electrolysis is an endothermic process. Of the 39 kWh theoretically required to form 1 kg of hydrogen gas, 33 kWh must be supplied in the form of electrical energy and 6 kWh must be supplied in the form of heat energy. Numerous catalysts are known to be capable of catalysing water electrolysis at voltages less than the thermoneutral cell potential for water electrolysis, which is 1.482 V at room temperature.

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[0190] However, all such catalysts only yield relatively low current densities at or below the thermoneutral potential at typical ambient temperatures. Accordingly, conventional water electrolyzers, which can only be operated in an economically-feasible way at high current densities cannot harness this effect with any sort of utility. They must necessarily operate at voltages well above the thermoneutral voltage, causing the formation of excess heat, which must then be removed at a further energy penalty.

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[0191] Even in cases where the cell operates at somewhat above the thermoneutral voltage, the cell may be sufficiently close to the thermoneutral voltage that the excess heat generated, along with additionally applied electrical heat, is such as to warm the cell up to a more optimum operating temperature and maintain it there without need for a formal or dedicated cooling system.

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[0192] These teachings have potentially important and far-reaching implications for the heat management, energy efficiency, and capital cost of electrochemical liquid-gas

cells. These options have not hitherto been available in conventional cells which only operate viably at high current densities. In particular, the new approaches teach that excess heat is a valuable resource that needs to be shepherded and conserved, not wasted.

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[0193] These realisations provide for:

- (1) A heat management system for an electrochemical cell that facilitates an endothermic reaction, where:
 - 10 i. The cell employs catalysts that are capable of catalysing the reaction below or near its thermoneutral cell voltage at ambient temperature, and
 - ii. The cell is maintained at or near a suitable temperature,
 - 15 iii. Where necessary, by the application of electrical heating, including, without limitation, electric resistive heater.
- (2) Optionally, the cell may be thermally insulated from the cell's surroundings by encasing the cell, either partially or fully, in a thermally insulating material(s).

20

High Current Density Operation

[0194] In example embodiments, methods for facilitating the operation of cells at high current densities, are described in the Applicant's concurrent International Patent
25 Application entitled "Electrochemical cell and components thereof capable of operating at high current density", filed on 14 December 2016, which is incorporated herein by reference.

[0195] In example embodiments, high current density is preferably greater than or
30 equal to 50 mA/cm². In other example embodiments, high current density is preferably greater than or equal to 100 mA/cm², greater than or equal to 125 mA/cm², greater than or equal to 150 mA/cm², greater than or equal to 200 mA/cm², greater than or equal to 300 mA/cm², greater than or equal to 400 mA/cm², greater than or equal to 500

mA/cm², greater than or equal to 1000 mA/cm², greater than or equal to 2000 mA/cm², or greater than or equal to 3000 mA/cm².

[0196] In such high current density operation, after cell adaption to this purpose, the
5 aforementioned cells may operate at substantially higher energy and electrical
efficiencies than are available for comparable, conventional cells. That is, the
advantages of example electrochemical cells as described herein, suitably adapted, may
be most strongly amplified at high current densities relative to a comparable
conventional cell. This discovery has important practical utility since many industrial
10 electro-synthetic and electro-energy cells aim to operate at the highest reasonable
current densities. Substantial energy and electrical savings may therefore be realised.

[0197] Moreover, for electrochemical reactions where high current densities and high
energy efficiencies are necessary in order to achieve economic viability, this discovery
15 can yield new industrial electro-synthetic and electro-energy processes that were
hitherto unavailable or unviable.

[0198] Adaption of the example electrochemical cells as described herein, including,
but not limited to cells of the types described in WO2013/185170, WO2015/013765,
20 WO2015/013766, WO2015/013767, and WO2015/085369, may involve special designs
for or modifications to the current collectors, busbars, electrical connections, power
supplies/receivers, and other components. For example, selected components within
the power supply of an electrosynthetic cell of the aforementioned types may be
specially designed in order to handle the high current densities. In example
25 embodiments, power supplies for facilitating the operation of cells of the above types,
are described in the Applicant's concurrent United States Provisional Application
entitled "DC power supply systems and methods", filed on 14 December 2016, which is
incorporated herein by reference. Similarly, novel current collectors such as
asymmetric conducting meshes may be used, if required, in order to effectively
30 distribute current at high current densities. One particular adaption involves the use of
series electrical connections as described in the Applicant's concurrent International
Patent Application entitled "Electrochemical cell and components thereof capable of

operating at high voltage”, filed on 14 December 2016, which is incorporated herein by reference.

[0199] In one example aspect, there is provided a spiral-wound electrochemical cell,
5 module or reactor capable of operating at high current density, having a core element,
around which one or more electrodes (e.g. at least one electrode pair provided by an
anode or a cathode) may be wound in a spiral fashion. The at least one electrode pair
can form part of a multi-electrode array, which can be considered as being comprised of
10 a series of flat flexible anodes and cathodes that can optionally be wound in a spiral
fashion. A “leaf” is comprised of one or more electrodes, for example an electrode, a
pair of electrodes, a plurality of electrodes, or some other form of electrode unit. A leaf
may be flexible and can be repeated as a unit. Thus, in one example the electrode(s) is
flexible, for example at least when being wound. After being wound, in some examples,
the electrode(s) might be hardened using a hardening process.

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[0200] For example, a leaf can include in part, or be formed by:

two electrodes, for example two cathodes or two anodes;
an electrode pair, for example an anode and cathode; or
a plurality of any of the above.

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[0201] In another example, a leaf can include in part, or be formed by, two electrode
material layers (with both layers together for use as an anode or a cathode) that are
positioned on opposite sides of an electrode gas channel spacer (i.e. a spacer material,
layer or sheet, which for example can be made of a porous polymeric material) which
25 provides a gas or fluid channel between the two electrodes.

[0202] Repeated leafs provide a multi-electrode array being a set of flat-sheet or spiral-
wound electrodes with intervening, electrically-insulating “flow-channel” spacers
between electrodes of different polarity (e.g. between an anode and a cathode)
30 providing separated liquid channels. The electrochemical cell, module or reactor may
optionally also involve end caps, and one or more external elements.

[0203] In example embodiments there is provided a core element and end caps for a spiral-wound electrochemical cell capable of facilitating high current densities, the core element, end caps, and/or external elements comprising or containing an electrically conductive element, such as a (primary) busbar, provided as the end cap; and wherein, 5 the conductive element is able to receive a conductive end from, or part of a conductive end from, or an electrode from, or a (secondary) busbar from an electrode, which may be a flexible electrode, where the electrode may be in a flat-sheet arrangement or may be spiral-wound about the core element. In another embodiment, the conductive element is able to provide a conductive lip to, or part of a conductive lip to, or an 10 electrode to, or a (secondary) busbar to an electrode, which may be a flexible electrode, where the electrode is optionally able to be spiral-wound about the core element.

[0204] In example embodiments, the current collectors of all anode electrodes are placed so as to overhang their electrodes on one side of the assembly of electrodes, leafs 15 or the like, while the current collectors of all the cathode electrodes are placed so as to overhang their electrodes on the opposite side to the anode electrodes. All of the overhanging anode electrodes are then combined into a single electrical connection, while all of the overhanging cathode electrodes are separately combined into a single electrical connection. If multiple leafs are connected by the approach, this method may 20 result in a parallel electrical connection of the leafs.

[0205] In these example aspects there are provided methods for forming the electrical connections with the flexible electrode leaf so as to thereby appropriately bring together, group, or aggregate electrodes in the leaf into single electrical fittings capable 25 of facilitating high current densities, for example, in a parallel electrical connection. These are preferably, but not exclusively, achieved by one of the means described below.

[0206] For example, one method involves interdigitating metallic wedges between 30 spiral current collectors extending off one end of the spiral-wound cell and then bringing the interdigitated wedges into electrical contact via a primary busbar with an attached connecting bus (*Wedge method*). In an alternative example, the current collector, interdigitated wedges and ring may be bolted together, in which case the

method is known as the “*Bolted Wedge Method*”: Alternatively, the current collectors, wedges and ring may be welded together, in which case the method is known as the “*Welded Wedge*” Method. The wedges may be narrowly disposed in finger-like projections off of the central ring, in which case the method is known as the “*narrow wedge method*”.
5 *wedge method*”. Alternatively, the wedges may be widely disposed, in which case the method is known as the “*wide wedge method*”.

[0207] Variations to the “*Wedge Method*”:

- 10 i. In these methods the overhanging current collectors from either the anode or cathode electrodes, leafs, or the like, are brought down into a collection of conductive powder (“*Powder Method*”) or small/microscopic spheres (“*Sphere Method*”), and a ring. Thereafter, the powder or spheres are placed in secure mechanical and electrical contact with the current collectors and the ring.
15 For example, the powder or spheres may be welded to the current collectors and the ring, thereby creating a primary busbar as an end cap of the cell.
- ii. “*Solder method*”: In this method the overhanging current collectors from either the anode or cathode electrodes, leafs, or the like, are brought down into a
20 powdered solder encircling a conductive ring. Thereafter, the solder is placed in secure mechanical and electrical contact with the current collectors and the ring by heating the assembly.
- iii. “*Continuous Wedge Method*”: In this variant, a wire, for example a square,
25 rectangular, triangular or flat wire, of suitable thickness is wound around the ring. The wire replaces the discrete wedges used in the “*Wedge Method*”. In effect, the wire forms a continuous wedge. The overhanging current collectors are brought down over the continuous wedge such that the current collectors interdigitate the continuous wedge, which fills the space between the current
30 collectors. Thereafter, the wire is placed in secure mechanical and electrical contact with the current collectors and the ring by, for example, welding the assembly.

- iv. “*Spiral Method*”: In this approach a primary busbar is manufactured by forming a spiral ledge into a circular conductor located at, or itself being, an end cap. The overhanging current collectors on the anode or cathode are formed to match the spiral ledge such that when the cell is spirally-wound, the overhanging current collectors fall on the ledge and can be securely and continuously welded to the ledge during the winding process.

[0208] These methods provide for:

- (1) An electrochemical cell for an electrochemical reaction, comprising:
- a wound electrode; and,
 - a busbar attached to a current collector of the electrode, where the current collector is spiral-wound, and
 - wherein the busbar is of such size and such design as to provide for operation of the cell at high current density.
- (2) A spiral-wound electrochemical cell for forming a chemical reaction product from an electrochemical reaction, the electrochemical cell comprising:
- an electrode spiral-wound about a central axis;
 - an end cap; and,
 - a busbar provided as part of the end cap;
 - wherein the busbar is attached to a current collector of the electrode, and the current collector is spiral-wound, and
 - wherein the busbar is of such size and such design as to provide for operation of the cell at high current density.

High Voltage Operation

- [0209] As described in the Applicant’s concurrent International Patent Application entitled “Electrochemical cell and components thereof capable of operating at high voltage”, filed on 14 December 2016 and incorporated herein by reference, example

electrochemical cells are disclosed for operation at high voltages. One example adaption involves arraying example cells in electrical series.

[0210] In example embodiments, high voltage is preferably greater than or equal to 2 V. In other example embodiments, high voltage is preferably greater than or equal to 3 V, greater than or equal to 5 V, greater than or equal to 10 V, greater than or equal to 25 V, greater than or equal to 50 V, greater than or equal to 100 V, greater than or equal to 250 V, greater than or equal to 500 V, greater than or equal to 1000 V, or greater than or equal to 2000 V.

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[0211] The series-connected cells are distinguished from spiral-wound and related, parallel-connected cells in that they allow for the use of substantially smaller and more readily connected primary busbars. Moreover, the cells allow for the use of a lower overall current but higher overall voltage than is generally utilized by related parallel-connected cells, including spiral-wound cells of the aforementioned type. This may be advantageous in that lower overall currents provide for lesser electrical resistance and therefore lesser (heat) losses, than higher overall currents. Moreover, power supplies which provide low overall current and high voltage are generally less expensive than power supplies which provide high overall current and low voltage. In example

embodiments, power supplies for facilitating the operation of series-connected cells of these types, are described in the Applicant's concurrent United States Provisional Application entitled "DC power supply systems and methods", filed on 14 December 2016, which is incorporated herein by reference.

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[0212] In other words, cells with series connections consume lower overall currents of higher overall voltage than cells with parallel connections that have the equivalent overall active electrochemical area and the same current density. In so doing, cells with series connections require smaller primary busbars than are necessary when large overall currents are required.

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[0213] Other advantages of a series arrangement in a cell include:

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- (1) it is typically simpler and less complex to connected busbars to series-connected cells than to their equivalent parallel-connected counterparts,
- (2) series-connected cells display an improved ability to handle large and sudden surges in current (since the system operates generally at lower overall currents), and
- (3) series-connected cells better allow for the use of current collectors of higher intrinsic resistance, since the overall current affects the overall resistance, which is related to the efficiency of the cell. A lower current yields a lower overall resistance, even with current collectors having a higher intrinsic resistance, thereby avoiding substantial penalty to the efficiency of the cell.

[0214] The disadvantages of series-connected cells relative to parallel-connected cells include the presence of parasitic currents.

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[0215] In an example embodiment there is provided a plurality of electrochemical cells for an electrochemical reaction. The plurality of electrochemical cells comprises a first electrochemical cell including a first cathode and a first anode, wherein at least one of the first cathode and the first anode is a gas diffusion electrode. The plurality of electrochemical cells also comprises a second electrochemical cell including a second cathode and a second anode, wherein at least one of the second cathode and the second anode is a gas diffusion electrode. Preferably, the first cathode is electrically connected in series to the second anode by an electron conduction pathway.

[0216] Preferably, chemical reduction occurs at the first cathode and the second cathode as part of the electrochemical reaction, and chemical oxidation occurs at the first anode and the second anode as part of the electrochemical reaction. In a particular example, the first cathode is a gas diffusion electrode. In another example, the first anode is a gas diffusion electrode. In another example, the second cathode is a gas diffusion electrode. In another example, the second anode is a gas diffusion electrode. In another example, an electrolyte is between the first cathode and the first anode. In another example, the electrolyte is also between the second cathode and the second anode.

[0217] Preferably, there is no diaphragm or ion exchange membrane positioned between the first cathode and the first anode. Also preferably, there is no diaphragm or ion exchange membrane positioned between the second cathode and the second anode.

- 5 In another example, in operation there is no voltage difference between the first cathode and the second anode. In another example, in operation there is a voltage difference between the first cathode and the second cathode.

- 10 [0218] In example operation of the cell, a first gas is produced at the first cathode, and substantially no bubbles of the first gas are formed at the first cathode, or bubbles of the first gas are not formed at the first cathode. Also in example operation of the cell, a second gas is produced at the first anode, and substantially no bubbles of the second gas are formed at the first anode, or bubbles of the second gas are not formed at the first anode.

- 15 [0219] Advantageously in another example, in operation the first gas is produced at the second cathode, and substantially no bubbles of the first gas are formed at the second cathode, or bubbles of the first gas are not formed at the second cathode, and, the second gas is produced at the second anode, and substantially no bubbles of the second gas are formed at the second anode, or bubbles of the second gas are not formed at the second anode.

- 25 [0220] Preferably, the first cathode is gas permeable and liquid impermeable. In an example embodiment, the first cathode includes a first electrode at least partially provided by a gas-permeable and electrolyte-permeable conductive material, and, a first gas channel at least partially provided by a gas-permeable and electrolyte-impermeable material. In another example embodiment, the first gas can be transported in the first gas channel along the length of the first cathode. In another example embodiment, the second anode includes a second electrode at least partially provided by a gas-permeable and electrolyte-permeable conductive material, and, a second gas channel at least partially provided by a gas-permeable and electrolyte-impermeable material. The second gas can be transported in the second gas channel along the length of the second anode.

[0221] In an example, the first gas channel is positioned to be facing the second gas channel. In another example, the first gas channel and the second gas channel are positioned between the first electrode and the second electrode. The first cathode and the second anode can be planar. The second cathode and the first anode can also be planar. The first cathode can be flexible, and the second anode can also be flexible.

[0222] In example embodiments, there are also provided convenient and efficient configurations, arrangements, or designs for electrically connecting flexible leafs in series; i.e. a multi-electrode array, within a flat-sheet electrochemical cell, module or reactor, and where each flexible leaf comprises of a sealed gas channel or channels with its associated electrode or electrodes.

[0223] In one set of example embodiments, double-sided electrode leafs are used. The leafs comprise of two electrode material layers positioned on opposite sides of an electrode gas pocket, containing a gas channel spacer (i.e. a spacer material, layer or sheet, which, for example, can be made of a porous polymeric material) that provides a gas or fluid channel between the two electrodes. The resulting gas pocket within the leaf is typically equipped with a gas port. The current collectors on the top-side of the double-sided electrode leafs are placed so as to overhang their electrodes on one side of the leaf, while the current collectors on the bottom-side of the leafs are placed so as to overhang their electrodes on the opposite side of the leaf. When the resulting leafs are uniformly stacked into a flat-sheet, multi-leaf arrangement, separated by liquid-permeable 'flow-channel' spacers, then electrical connections are made by combining overhanging current collectors in pairs on either side of the stack. That is, the top electrode of one leaf is connected to the top electrode on the leaf above or below it, whilst the bottom electrodes of the two leafs are also separately connected to each other on the other side of the stack. This connection methodology is continued down the full length of the stack of leafs, so that all of the leafs in the stack are connected to another leaf in a pairwise arrangement. Multiple leafs connected by the approach result in a series electrical connection of the electrodes in the stack. When the volumes between the leafs are filled with a liquid or gel electrolyte, then the resulting cell is known as a "side-connected series cell".

[0224] In further example embodiments, electrode leafs comprise of two separate, adjoining gas pockets, each having its associated porous electrode located on its outside (i.e. on the opposite side to the adjacent gas pocket). The resulting leaf, which may be flexible, then comprises of a layered arrangement having an electrode on its top, with one gas pocket below it, followed by a second, separate gas pocket below that, followed by a second electrode below it, on the bottom of the leaf. The gas pockets may each contain a gas-channel spacer within them to hold them up, and will typically each be equipped with a gas port. The two porous electrodes at the top and bottom of the leaf are then electrically connected to each other by, for example, metallic interconnections that pass through the two gas pockets, or that pass around the sides of the two gas pockets. The two gas pockets in each such leaf are sealed from each other, meaning that gas in one pocket is not able to pass into the adjoining pocket, and vice versa. Double-sided, double-gas pocketed leafs of this type are then stacked on top of each other with a liquid-permeable “flow-channel” spacer between them, to thereby create a multiple-leaf, series-connected “stack”. When the volumes between the leafs are filled with a liquid or gel electrolyte, then the resulting cell of this type is known as a “bipolar series cell”.

[0225] A key advantage that series-connected cells of this type have over comparable parallel-connected cells, such as the spiral-wound cells mentioned above, involves the way in which they are connected to their primary busbars.

[0226] The upper-most electrode of the upper-most leaf in each of the aforementioned stacks will typically be connected along its length to a primary busbar, which will typically take the form of a metallic bar that runs along one edge of the top of the stack. The lower-most electrode of the lower-most leaf will typically be separately connected along its length to a second primary busbar, which may take the form of a metallic bar that runs along one edge of the bottom of the stack. The two busbars will typically form the connection points (positive and negative poles) to which an external power supply will be connected. As noted above, because of the lower overall current and higher overall voltage of such a stack, each busbar will typically contain less metal and be smaller overall than a busbar in a comparable, parallel-connected stack of the same overall electrochemical active surface area at the same current density (such as a spiral-

wound cell of the aforementioned type). Moreover, because the busbar are linear rods, they will typically also be simpler to connect to electrically using a means such as welding. There will typically not be a need to use complex techniques for busbar attachment, such as the aforementioned ‘*Wedge Method*’, ‘*Bolted Wedge Method*’,
5 ‘*Welded Wedge Method*’, ‘*Narrow or Wide Wedge Method*’, ‘*Powder Method*’, ‘*Sphere Method*’, ‘*Solder method*’, ‘*Continuous Wedge Method*’, or ‘*Spiral Method*’.

[0227] In still further examples, series-connected leaf stacks may be wound into a spiral-wound cell. A “tricot” pack of porous flow-channel spacers may be constructed
10 to accommodate a selected number of leafs, whose gas pocket/s are each equipped with a gas port, in a stack. The tricot pack and leafs are then wound about a central core element that has been adapted to connect the gas ports on each leaf to their relevant gas conduits within the core element. In the case where leafs comprising double-sided electrodes enclosing a single gas pocket are used, pairwise electrical connections of
15 upper and lower electrodes on adjacent leafs are made on opposite sides of the leaf stack following the spiral winding, to thereby produce a “side-connected series cell” having a spiral-wound architecture. In the case where leafs comprising double-sided electrodes enclosing two adjacent gas pockets (with electrical interconnections between the upper and lower electrodes), the resulting assembly provides a “bipolar series cell”
20 having a spiral-wound architecture.

[0228] These approaches provide for:

- (1) An electrochemical cell for an electrochemical reaction, comprising:
25
 - a stack of electrode leafs;
 - separated from each other by intervening, electrically-insulating liquid-permeable spacers;
 - wherein the individual leafs are connected to each other in a series electrical arrangement.
- (2) An electrochemical cell for an electrochemical reaction, comprising:
30
 - a stack of electrode leafs connected in electrical series; wherein:

- a primary busbar is electrically attached to the upper-most electrode in the upper-most leaf in the stack, and
- a separate primary busbar is electrically attached to the bottom-most electrode in the bottom-most leaf in the stack,
- 5 - wherein the busbar is of such size and such design as to provide for operation of the cell at high current density.

FURTHER EXAMPLES

- 10 [0229] The following further examples provide a more detailed discussion of particular embodiments. The further examples are intended to be merely illustrative and not limiting to the scope of the present invention.

Example 1: Void Volumes and their Placement

- 15 [0230] Preferably but not exclusively, a void volume(s) is provided by a porous structure that is not permeable to an electrolyte, e.g. a liquid electrolyte, but accommodates or allows passage of gas, that is the porous structure is liquid-impermeable and gas permeable. In the case of an aqueous liquid electrolyte, the void
- 20 volume(s) is preferably but not exclusively provided by a porous hydrophobic structure, e.g. made of PTFE, such as a porous hydrophobic assembly, membrane or hollow fibre, or a collection of such structures, which remains unfilled with liquid electrolyte during the operation of the cell. In such cases, the void volume may be considered to be an
- 25 “artificial bubble” or a “man-made bubble”. Preferably the “artificial bubble” or “man-made” bubble lies outside of the electrical conduction pathway of the cell, or occupies only a small cross-sectional area or footprint within the electrical conduction pathway.

- [0231] In alternative preferred embodiments, a void volume can be provided by a natural bubble or bubbles that are statically or near-statically positioned outside of, or
- 30 within a small cross-sectional area or footprint in the conduction pathway of the cell. For example, the static or near-static, natural bubble or bubbles may be contained, or mechanically trapped within an accommodating structure that is located outside of, or within a small cross-sectional area or footprint within the conduction pathway of the

cell. In another example, the natural, static or near-static bubble or bubbles may simply be formed or located outside of, or within a small cross-sectional area or footprint in the conduction pathway of the cell.

- 5 [0232] In one embodiment, an electrochemical cell contains one or more void volumes that are so configured as to accept and accommodate migrating gas so as to thereby improve the efficiency of the cell.

[0233] Referring to Figure 4, for example, an electrochemical cell 100 with an aqueous
10 liquid or gel electrolyte 105 between anode 110 and cathode 120 may include one or more sheets of membrane 130, for example short portions of a thin, highly hydrophobic sheet membrane, or hollow fibre membrane, that is isolated and not in gaseous contact or communication with the environment about membrane 130. Membrane 130 provides one or more void volumes. Isolated portions of a thin, highly hydrophobic sheet
15 membrane, or hollow fibre membrane, can be placed so as to accept and accommodate gas that is slowly but inopportunately generated within the cell during operation. In addition to being isolated from the surroundings, the voids within the hydrophobic membranes may also be isolated from each other and, or they may be in gaseous contact with each other.

20

[0234] The membranes 130 can be located at or near position 140 provided by the edges or walls of the cell 100, that is, outside of, or at the periphery of, the electrical conduction pathway (e.g. conduction pathways are illustrated by area 125 in Figure 5) which is between the electrodes, which are preferably gas-producing electrodes.
25 Alternatively or additionally, the hydrophobic membranes 130 can be placed in, for example, a lengthwise location or position 150, which is parallel to or substantially parallel to, or along, the electrical conduction pathway, to thereby minimise the cross-sectional area or footprint of membranes 130 for reduced or minimal electrical resistance. Position or location 150 of membranes 130 can also be considered as
30 perpendicular, or substantially perpendicular, to one or more of the gas-producing electrodes, i.e. perpendicular to anode 110 and/or perpendicular to cathode 120.

[0235] For example, suitable porous structures or membranes that provide the void volume(s) may accommodate gas that is slowly but inopportunately created within a battery during overcharging, including but not limited to a Ni metal hydride, lead acid, or lithium ion battery, where the uncontrolled formation of independent gas bubbles has the potential to damage the battery or degrade its performance. In such an application, the void volumes may, in effect, replace or partially replace the sacrificial materials that are routinely incorporated to suppress gas formation in battery electrolytes or electrode coatings. The void volume(s) may further act as a “buffer tank” to hold amounts of gases that are formed prior to the reverse, recombination reaction that removes them during discharging.

[0236] In another example, the void volume(s) may accommodate gas formed during the operation of an electrophoretic or electroosmotic cell to thereby improve the operation of the cell. In further non-limiting examples, the void volume(s) may act to halt or minimise the incidence of bubble formation in electrochemical cells with solid-state or gel electrolytes. Preferably, there are substantially no bubbles of gas produced at the gas-producing electrodes.

[0237] In example forms, the one or more void volumes are: positioned within, partially within or adjacent to the electrolyte; and/or located at or adjacent to one or more of the gas-producing electrodes.

[0238] It is to be understood that, even in cases where a void volume(s) is in gaseous isolation from its environment within a liquid media, the void volume(s) can still be capable of accepting substantial quantities of gas. This may arise because a void volume(s) will necessarily and competitively accommodate migrating gas up to the point that the internal gas pressure within the void volume exceeds the so-called “bubble point” of the void volume. At that stage one or more bubbles will form in an uncontrolled manner at the interface between the void volume and the surrounding liquid media. Thus, the fact that a void volume(s) may be in gaseous isolation within a liquid or gel media does not prevent the void volume(s) from accepting and accommodating even substantial quantities of gas.

[0239] In a second preferred embodiment, the membrane(s) providing the void volume(s) does not merely accept and accommodate migrating gas, but additionally or instead forms a gaseous conduit that transports the migrated gas from/to another part of the cell, or into/out of the cell entirely. For example, the void volume(s) can act to
5 allow unwanted gases formed within the electrolyte of the cell to escape from the cell.

[0240] Referring to Figure 5, for example, membrane 160, providing one or more void volume(s), can transport gas from the electrolyte 105 present between the gas-producing electrodes 110, 120 to another portion 180 of the cell 100 that lies outside of,
10 or substantially outside of the conduction pathway (e.g. conduction pathways are illustrated by area 125) of the cell 100, or to the outside 170 of the cell 100.

[0241] Thus, in examples there is provided an electrochemical cell 100 for producing a gas from an electrochemical reaction, comprising one or more void volumes 130, 160, a
15 gas-producing electrode 120, a counter electrode 110, and an electrolyte 105 at least between the gas-producing electrode 120 and the counter electrode 110. In operation an intermittent or fluctuating current is supplied to at least the gas-producing electrode 120, and the gas is produced at the gas-producing electrode 120 and is received by the one or more void volumes 130, 160.

20 [0242] For example, the membrane(s) 160 providing the void volume(s) can be placed so as to provide a pathway for gas that is slowly but inopportunistically created within the electrolyte between the gas-producing electrodes. For example, in a battery during overcharging, including but not limited to a Ni metal hydride, lead acid, or lithium ion
25 battery, where the uncontrolled formation of independent gas bubbles has the potential to damage the battery or degrade its performance. In such an application, the void volumes may, in effect, replace or partially replace the sacrificial materials that are routinely incorporated to suppress gas formation. The void volume(s) may transport the gas to a volume within the cell that acts as a “buffer tank” to hold amounts of gases that
30 are formed prior to the reverse, recombination reaction that removes them during discharging.

[0243] In another example, the membrane(s) 160 providing the void volume(s) can transport gas from the electrolyte 105 between the gas-producing electrodes 110, 120 to

another portion 180 of the cell 100 that lies outside of the electrical conduction pathway of the cell, or to the outside 170 of the cell. For example, during the operation of an electrophoretic or electroosmotic cell to thereby improve the operation of the cell. In further non-limiting examples, void volume(s) of this type may act to halt or minimise the incidence of bubble formation in electrochemical cells with solid-state or gel electrolytes.

[0244] In other examples, the void volume(s) can act to continuously remove dissolved gases within a liquid- or gel-electrolyte of an electrochemical cell between the gas-producing electrodes, to thereby improve the electrical conductivity and hence the electrical efficiency of the cell. That is, the void volume(s) can be used to continuously “de-gas” the electrolyte and vent dissolved gases to the air, so as to thereby improve the electrical conductivity of the electrolyte.

[0245] Thus, Figure 4 and Figure 5 provide example positions for one or more void volumes, e.g. a porous structure, a pre-existing bubble, gas region or gas pathway. In one example, the one or more void volumes, provided by example membranes 130, 160, can be positioned, at or near position 140, outside of the electrical conduction pathway between the gas-producing electrodes (i.e. anode 110 and cathode 120). Alternatively or additionally, the one or more void volumes, provided by example membranes 130, 160, can be positioned, at or near position 140, substantially outside of the electrical conduction pathway between the electrodes. Alternatively or additionally, the one or more void volumes, provided by example membranes 130, 160, can be positioned, at or near position 140 or outside position 170, partially outside of the electrical conduction pathway between electrodes. Alternatively or additionally, the one or more void volumes, provided by example membranes 130, 160, can be positioned, at or near position 140, peripheral to or adjacent to the electrical conduction pathway between electrodes. Alternatively or additionally, the one or more void volumes, provided by example membranes 130 can be positioned, at or near position 150, between the electrodes and within the electrical conduction pathway, but having a small cross-sectional area relative to the electrical conduction pathway between electrodes. Alternatively or additionally, the one or more void volumes, provided by example membranes 130 can be positioned, at or near position 150, between the electrodes and

parallel to the electrical conduction pathway, so as to have a small cross-sectional area relative to the electrical conduction pathway between electrodes. Alternatively or additionally, the one or more void volumes, provided by example membranes 130 can be positioned, at or near position 150, between the electrodes and perpendicular to one or both of the electrodes, so as to have a small cross-sectional area relative to the electrical conduction pathway between electrodes. In further examples, the one or more void volumes, provided by example membranes 130, 160 can be positioned, at or near position 140 and/or position 150, to be within, partially within, adjacent to or near to a liquid electrolyte, or gel electrolyte of the cell. Alternatively or additionally, the one or more void volumes, provided by example membranes 130, 160, can be positioned, at, next to or adjacent to an electrode, and outside of the electrical conduction pathway between the electrodes, for example positioned substantially parallel to one or more of the electrodes and on the gas side of the one or more electrodes.

[0246] In other examples, the void volume(s) can act to competitively suppress dissolution of gas within an electrolyte, so as to thereby maximise the electrical conductivity of the electrolyte. In additional examples, the void volume(s) can act to carry a particular inert gas into the cell, so as to thereby saturate the electrolyte with a gas that is reactively inert and to thereby improve the overall efficiency of the cell.

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[0247] Thus there is provided an electrochemical cell having an electrolyte between gas-producing electrodes of the electrochemical cell, wherein the electrolyte is a liquid-electrolyte or a gel-electrolyte. The electrochemical cell comprises one or more void volumes to receive a gas produced by the electrochemical cell, and wherein dissolution of the gas in the electrolyte is reduced or avoided by the one or more void volumes. Furthermore, bubbles of the gas are not produced at the gas-producing electrodes.

25

[0248] The one or more void volumes can be positioned within, partially within or adjacent to the electrolyte in example forms. In one example, the one or more void volumes facilitate migration of the gas to the one or more void volumes so that:

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- the Electrolyte Factor (EF) is increased/maximized;
- the Power Density Factor (PF) is reduced/minimized; and
- the Crossover (CO) is reduced/minimized.

[0249] In one example, the one or more void volumes transport gas from the electrolyte to another portion of the cell that lies outside of the conduction pathway of the cell. In another example, the one or more void volumes transport gas from the electrolyte to outside of the cell. In another example, the one or more void volumes transport an inert gas into the cell.

[0250] In another example, the one or more void volumes are provided by a porous structure that is permeable to the gas and impermeable to the electrolyte. In another example, the one or more void volumes are provided by a porous structure that is gas-permeable and liquid-impermeable. In another example, the one or more void volumes are provided by a porous hydrophobic structure which remains unfilled with electrolyte during operation of the cell.

[0251] In another example, the one or more void volumes are a pre-existing bubble, a gas region or a gas pathway. In another example, the one or more void volumes are provided by at least one natural bubble that is statically positioned by an accommodating structure.

[0252] In another example, the one or more void volumes are positioned outside of the electrical conduction pathway between the electrodes. In another example, the one or more void volumes are positioned partially outside of the electrical conduction pathway between the electrodes. In another example, the one or more void volumes are positioned peripheral to the electrical conduction pathway between the electrodes. In another example, the one or more void volumes are positioned between the electrodes and parallel to the electrical conduction pathway between the electrodes. In another example, the one or more void volumes are positioned between the electrodes and perpendicular to one or both of the electrodes.

[0253] In another example, the one or more void volumes are integrally formed as part of at least one electrode. In another example, the one or more void volumes are positioned at or adjacent to at least one electrode. In another example, the one or more void volumes at least partially form a gaseous side of a gas diffusion electrode.

[0254] In another example, at least one electrode of the electrochemical cell comprises a non-conductive gas permeable material that is substantially impermeable to the electrolyte and provided on a gas side of the at least one electrode, and a porous conductive material provided on an electrolyte side of the at least one electrode.

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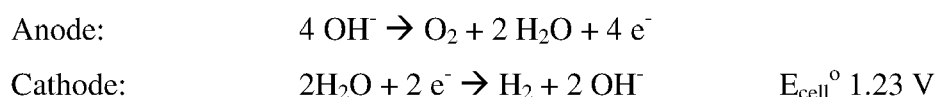
Example 2: Applying large and fluctuating currents to a water electrolysis cell

[0255] In a further preferred embodiment, the void volume may be associated with an electrode. That is, the void volume may form the gaseous side of a gas diffusion
10 electrode, where the gaseous side of the electrode lies outside of, or substantially outside of the conduction pathway of the cell between the electrodes, and where the gaseous side of the gas diffusion electrode facilitates the movement of gas into or out of the cell. The gas diffusion electrode may act to transport a gas generated rapidly and suddenly at the electrode out of the cell. Examples of such cells include an
15 electrosynthetic or an electro-energy cell.

[0256] Example electrochemical cells as described herein, and including but not limited to cells of the types described in WO2013/185170, WO2015/013764, WO2015/013765, WO2015/013766, WO2015/013767, WO2015/085369, all of which
20 are incorporated herein by reference, can be modified to operate at high current density as described in the Applicant's concurrent International Patent Application entitled "Electrochemical cell and components thereof capable of operating at high current density", filed on 14 December 2016, which is incorporated herein by reference.

[0257] In example embodiments, the electrochemical cell accommodates random, sudden or rapid and large increases in the current or the current density. In example embodiments, a large increase in the current is preferably more than double the existing, base, stable or previous operating current. In alternative example
25 embodiments, a large increase in the current is preferably more than triple the current, more than four-fold the current, more than five-fold the current, more than six-fold the current, more than eight-fold the current, more than ten-fold the current, more than twelve-fold the current, more than fifteen-fold the current, more than twenty-fold the current, or more than twenty-five-fold the current.
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[0258] To illustrate operation of this type, consider Figure 6, which schematically depicts an example embodiment for a water electrolyzer, containing two gas diffusion electrodes, being an anode and a cathode. The standard operating current for the electrolyzer is 10 mA (or expressed as a current density is: 10 mA/cm²). For illustrative purposes, the cell is an alkaline electrolyser; that is, the cell facilitates electrochemical water-splitting, with half reactions as shown below, in alkaline solution, containing aqueous potassium hydroxide, aq. KOH, as electrolyte. (An acid or a neutral electrolyte could alternatively be used, with suitable catalysts).



[0259] The electrochemical cell 1000 in Figure 6 comprises the following parts: a central water reservoir 1100 has a water-free hydrogen collection chamber 1110 on the left side and a water-free oxygen collection chamber 1120 on the right side. Between the water reservoir 1100 and the hydrogen collection chamber 1110 is a gas diffusion electrode 1130. Between the water reservoir 1100 and the oxygen collection chamber 1120 is a gas diffusion electrode 1140. On or close to the surface of the gas diffusion electrodes 1130 and 1140 is a conductive layer containing a suitable catalyst 1150. In one example, the catalyst 1150 is a mixture of nickel nano- and microparticles (90% by weight) with PTFE (10%). When an electrical direct current is applied to the conductive layers 1150 by the battery 1160, then electrons flow along the outer circuit 1170. The current causes water to be split into hydrogen at the gas diffusion electrode 1130 (the cathode) and oxygen at the gas diffusion electrode 1140 (the anode). Instead of forming bubbles at these surfaces, the oxygen and hydrogen passes through the hydrophobic pores 1180 of the gas diffusion electrodes into the oxygen and hydrogen gas collection chambers 1120 and 1110, respectively. Liquid water cannot pass through these pores since the hydrophobic surfaces of the pores of the gas diffusion electrode and the surface tension of the water prevents droplets of water from disengaging from the bulk of the water to thereby pass through the pores. Thus, the gas diffusion electrodes 1130 and 1140 act as a gas-permeable, water-impermeable barrier.

- [0260] An electrochemical cell of the type shown in Figure 6 was subjected to a highly fluctuating applied current, supplied to the electrodes, having the profile depicted in Figure 7. As can be seen, the current profile rapidly and repeatedly fluctuates very suddenly between a current of 5 mA (which in the present example system corresponds to an equivalent current density of 5 mA/cm²) and a current of 250 mA (which in the present example system corresponds to an equivalent current density of 250 mA/cm²). Note that the profile occupies 2 minutes of time. The profile was applied repeatedly and continuously to the electrochemical cell of Figure 6 for a total of 55 days.
- 10 [0261] At one particular, invariant 2 minute time period during each 24 hours, the voltage produced by the electrochemical cell at the points marked A-D in Figure 7 was measured. Figure 8 depicts the resulting data over the 55 days of measurement.
- 15 [0262] As can be seen, despite being subjected to an aggressively fluctuating and intermittent current that changed over short, very short or extremely short periods of time, the liquid containing electrolysis cell handled the gases generated and the changes in current very well indeed. In fact, the data indicates excellent stability in the electrochemical cell over the extended testing period
- 20 [0263] The normal operating current for the electrochemical cell was 10 mA. Thus, the data at point B (250 mA) in Figure 7 represents a 25-fold larger current than the normal operating current. To the best of the inventors' knowledge no gas-liquid electrochemical cell, much less a liquid-containing electrochemical cell, is capable of such a feat.
- 25 [0264] It is worth also noting that the "rise"-time and "fall"-time for some of the fluctuations shown in Figure 7 are in the order of microseconds. Despite so rapid a fluctuation, the cell handled the changes without any difficulties.
- 30 [0265] This example demonstrates an electrochemical cell and a method for operating the electrochemical cell, wherein the electrochemical cell comprises a gas-producing electrode, a counter electrode, and where the gas-producing electrode and the counter electrode are separated by the electrolyte. Also provided is one or more void volumes, in this case at or adjacent to the electrodes. The method comprises supplying the

fluctuating current to at least the gas-producing electrode, and producing a gas (H₂ or O₂) at the gas-producing electrode as a result of the electrochemical reaction. The gas is received by the one or more void volumes.

5 Example 3: Applications in industrial / commercial electrochemical cells

[0266] It will be understood by persons skilled in the art that gas-liquid electrochemical cells capable of handling large and sudden fluctuations and intermittency in current have important practical applications in, for example, directly harnessing intermittent
10 energy sources, like solar-powered or wind-powered or ocean wave/tidal-powered renewable electricity, without notable modulation or conditioning of the current (direct or alternating depending on the energy source). For example, instead of converting the electrical current output of a solar-generator or wind-generator into alternating current of near-uniform intensity, the raw output of intermittent current produced by such a
15 generator can be directly harnessed by or supplied to an electrochemical cell of the present embodiments. This potentially eliminates a number of energy losses, allowing for more efficient use of renewable energy streams, such as solar-generators or wind-generators or ocean wave/tidal-generators.

20 [0267] For example, with use of present embodiments, intermittent power of this type can be practically employed in the electrochemical manufacture of a host of standard industrial products, including, but not exclusively: (a) chlorine, (b) hydrogen peroxide, (c) ozone, (d) caustic (with or without chlorine), (e) potassium permanganate, (f) chlorate, (g) perchlorate, (h) fluorine, (i) bromine, (j) persulfate, (k) fuels from CO₂, (l)
25 CO₂ from methane, and others.

[0268] In alternative examples, electrochemical cells involving electrochemical processes unique to particular industries can be powered by intermittent renewable energy sources, including but not restricted to:

- 30 (i) electrometallurgical applications, such as metal electrowinning;
(ii) pulp and paper industry applications, such as: (a) “*black liquor*” electrolysis, (b) “*Tall Oil recovery*” and (c) chloride removal electrolysis.

[0269] A large range of potential industrial and/or commercial electrochemical processes may benefit by use of present embodiments.

Example 4: Application involving fluctuating or intermittently supplied fuels and feedstocks

[0270] In another example aspect, electrochemical cells can be used to generate electrochemical energy, where the fuel for the energy may only be supplied intermittently, sporadically, or in a highly fluctuating manner. For example, fuel cell and related device applications, such as hydrogen-oxygen fuel cells, including but not limited to alkaline fuel cells, where the fuel (in the form of the gases oxygen and hydrogen) is supplied in a fluctuating, intermittent or highly variable manner, can be realised.

[0271] Similarly, half fuel cells, where, for example, only one of the electrodes is a gas diffusion electrode, can be enabled in cases where the gas feedstock required for that electrode is available only in a fluctuating, intermittent or highly variable manner. For example, the gas diffusion electrode may be an air electrode, which utilizes the oxygen in air. In cases where that electrode may receive only fluctuating, intermittent or highly variable amounts of air, present embodiments can enable the electrochemical cell to nevertheless operate efficiently.

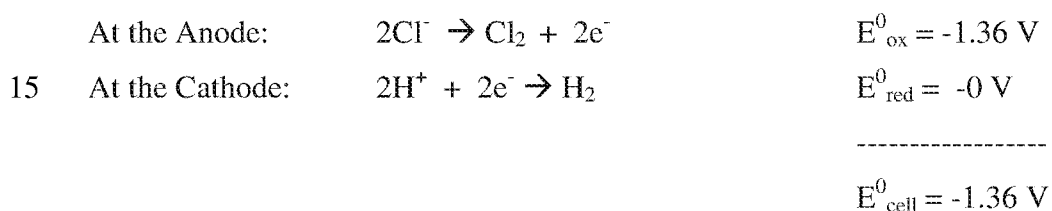
Example 5: Applications to electrochemical recycling or disposal

[0272] In further example aspects, electrochemical cells of present embodiments can be used to facilitate improved recycling or disposal of unwanted materials. For example, the joint venture company UhdeNora have developed an electrochemical technique for recycling the hydrochloric acid waste product that often derives from the industrial use of chlorine, Cl_2 , back into usable chlorine Cl_2 . The UhdeNora cell comprises a gas diffusion cathode combined with a standard solid-state (dimensionally-stable) chlorine-generating anode. According to reports, the UhdeNora cell routinely operates at 1.4 V and 500 mA/cm^2 , giving an energy requirement of 1.06 kWh per kg of chlorine produced. The UhdeNora cell could not operate efficiently (or likely without damage)

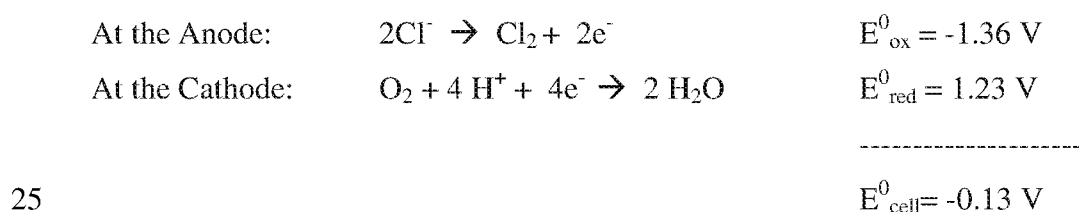
using a highly intermittent and fluctuating power source, like a solar-generator or wind-generator, directly connected to the cell.

[0273] In an example application, an electrochemical cell of a present embodiment can be employed instead, the cell having two gas diffusion electrodes, an anode and a cathode. There are two options to operate such a cell. In both options, the anode produces chlorine gas. In the first option, the cell is operated with hydrogen (H₂) generated at the cathode. In the second option, the cathode (a gas diffusion electrode) has O₂ (including, potentially, air O₂) introduced into the cathode, causing the cathode to act as an oxygen-depolarized cathode.

[0274] The half reactions in the former process are:



[0275] The half-reactions in the latter process, involving an oxygen depolarized cathode, are as follows:



[0276] As can be seen, the cell voltage is 1.36 V in the former case and a mere 0.13 V in the latter case. In both of these cases, the cell voltage is substantially less than the conventional chlor-alkali process.

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[0277] An electrochemical cell of present embodiments could carry out either of the above transformations using current directly from an intermittent and/or fluctuating power source, such as a solar-generator or a wind-generator, and where the current can

be unconditioned. This not only enables a more efficient use of renewable energy sources, but also enables their on-site use in a way that has not been previously viable.

Example 6: Applications to the management of electrical grids

5 [0278] Electrochemical cells of present embodiments can also be used to facilitate improved management of electrical grids that receive notable inputs from one or more intermittent energy sources, such as solar-powered or wind-powered or ocean wave/tidal-powered renewable electricity. Because of the fluctuating nature and
10 intermittency of such energy sources, electrical grids containing large inputs from renewables may generate excesses, including large excesses, of unwanted electrical power, at specific times. These times can be sporadic or short. These times may, alternatively, be long-lived. On occasion, this may result in the cost of the energy becoming negative, that is, the electrical utility may have so much unwanted energy
15 that it will pay for a user to consume the electricity.

[0279] In order to help balance the grid and avoid such unwanted excesses, electrochemical cells can be used that may, for example, manufacture useful materials that can be sold separately and thereby make good use of the excess energy. Such
20 electrochemical cells would necessarily have to be able to effectively harness fluctuations and intermittency in the supplied power. The present example electrochemical cells are able to achieve this result. Accordingly, electrochemical cells of present embodiments can be used to make good use of fluctuating and intermittent unwanted excesses of electrical energy that may become available on an electric grid
25 and that would otherwise be wasted so as to thereby help balance and stabilize the grid. Other potential applications include intermittent power generation to compensate for intermittency elsewhere in the grid or in user profiles.

[0280] Throughout this specification and the claims which follow, unless the context
30 requires otherwise, the word "comprise", and variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

[0281] Optional embodiments may also be said to broadly consist in the parts, elements and features referred to or indicated herein, individually or collectively, in any or all combinations of two or more of the parts, elements or features, and wherein specific integers are mentioned herein which have known equivalents in the art to which the invention relates, such known equivalents are deemed to be incorporated herein as if individually set forth.

[0282] Although a preferred embodiment has been described in detail, it should be understood that many modifications, changes, substitutions or alterations will be apparent to those skilled in the art without departing from the scope of the present invention.

The claims.

1. A method for operating an electrochemical cell, wherein the electrochemical cell comprises:
 - one or more void volumes;
 - a gas-producing electrode; and,
 - a counter electrode, the gas-producing electrode and the counter electrode being separated by an electrolyte;wherein the method comprises:
 - supplying an intermittent or fluctuating current to at least the gas-producing electrode; and
 - producing a gas at the gas-producing electrode as a result of an electrochemical reaction, wherein the gas is received by the one or more void volumes.
2. The method of claim 1, wherein the electrolyte is a liquid electrolyte.
3. The method of claim 1, wherein the electrolyte is a gel electrolyte.
4. The method of any one of claims 1 to 3, wherein substantially no bubbles of the gas are formed at the gas-producing electrode, or bubbles of the gas are not formed at the gas-producing electrode.
5. The method of any one of claims 1 to 4, wherein the current is unconditioned.
6. The method of any one of claims 1 to 5, wherein the current is derived from excess electrical energy from an electrical grid.
7. The method of any one of claims 1 to 6, wherein there is no ion exchange membrane positioned between the gas-producing electrode and the counter electrode.
8. The method of any one of claims 1 to 6, wherein there is no diaphragm positioned between the gas-producing electrode and the counter electrode.

9. The method of any one of claims 1 to 8, wherein the gas-producing electrode is a gas diffusion electrode.

10. The method of any one of claims 1 to 9, wherein the counter electrode is a gas diffusion electrode.

11. The method of any one of claims 1 to 10, wherein the counter electrode produces a second gas, and substantially no bubbles of the second gas are formed at the counter electrode, or bubbles of the second gas are not formed at the counter electrode.

12. The method of claim 11, wherein the second gas is received by separate one or more void volumes.

13. The method of any one of claims 1 to 12, wherein the current fluctuates by more than double the current.

14. The method of any one of claims 1 to 13, wherein the current fluctuates by:

- more than triple the current,
- more than four-fold the current,
- more than five-fold the current,
- more than six-fold the current,
- more than eight-fold the current,
- more than ten-fold the current,
- more than twelve-fold the current,
- more than fifteen-fold the current,
- more than twenty-fold the current, or
- more than twenty-five-fold the current.

15. The method of any one of claims 1 to 14, wherein the one or more void volumes are positioned within, partially within or adjacent to the electrolyte.

16. The method of any one of claims 1 to 14, wherein the one or more void volumes are positioned at or adjacent to the gas-producing electrode.

17. An electrochemical cell for producing a gas from an electrochemical reaction, comprising:

one or more void volumes;

a gas-producing electrode;

a counter electrode; and,

an electrolyte between the gas-producing electrode and the counter electrode;

wherein in operation an intermittent or fluctuating current is supplied to at least the gas-producing electrode; and

wherein the gas is produced at the gas-producing electrode and is received by the one or more void volumes.

18. The electrochemical cell of claim 17, wherein the electrolyte is a liquid electrolyte or a gel electrolyte.

19. The electrochemical cell of claim 17 or 18, wherein substantially no bubbles of the gas are formed at the gas-producing electrode, or bubbles of the gas are not formed at the gas-producing electrode.

20. The electrochemical cell of any one of claims 17 to 19, wherein the one or more void volumes form a gaseous conduit to transport the gas.

21. The electrochemical cell of any one of claims 17 to 20, wherein the one or more void volumes allow the gas if formed rapidly in the electrolyte to escape from the electrochemical cell.

22. The electrochemical cell of any one of claims 17 to 21, wherein there is no diaphragm or ion exchange membrane positioned between the gas-producing electrode and the counter electrode.

23. The electrochemical cell of any one of claims 17 to 22, wherein the gas-producing electrode is a gas diffusion electrode.

24. The electrochemical cell of any one of claims 17 to 23, wherein the counter electrode is a gas diffusion electrode.

25. The electrochemical cell of any one of claims 17 to 24, wherein the one or more void volumes are positioned within, partially within or adjacent to the electrolyte.

26. The electrochemical cell of any one of claims 17 to 24, wherein the one or more void volumes are positioned at or adjacent to the gas-producing electrode.

27. The electrochemical cell of any one of claims 17 to 24, wherein the one or more void volumes are positioned:

outside of the electrical conduction pathway between the gas-producing electrode and the counter electrode, or

peripheral to or adjacent to the electrical conduction pathway between the gas-producing electrode and the counter electrode.

28. The electrochemical cell of any one of claims 17 to 24, wherein the one or more void volumes are positioned between the gas-producing electrode and the counter electrode and within the electrical conduction pathway.

29. The electrochemical cell of any one of claims 17 to 24, wherein the one or more void volumes have a small cross-sectional area relative to the electrical conduction pathway between the gas-producing electrode and the counter electrode.

30. The electrochemical cell of any one of claims 17 to 24, wherein the one or more void volumes are positioned perpendicular to one or both of the gas-producing electrode and the counter electrode.

31. The method of any one of claims 17 to 30, wherein the current is produced by an intermittent or fluctuating power source.

32. The method of claim 31, wherein the power source is a solar-generator or a wind-generator.

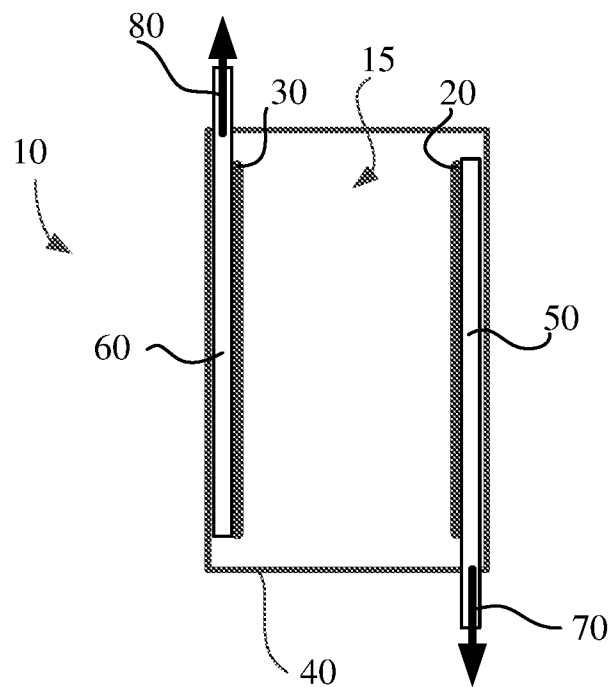


FIGURE 1

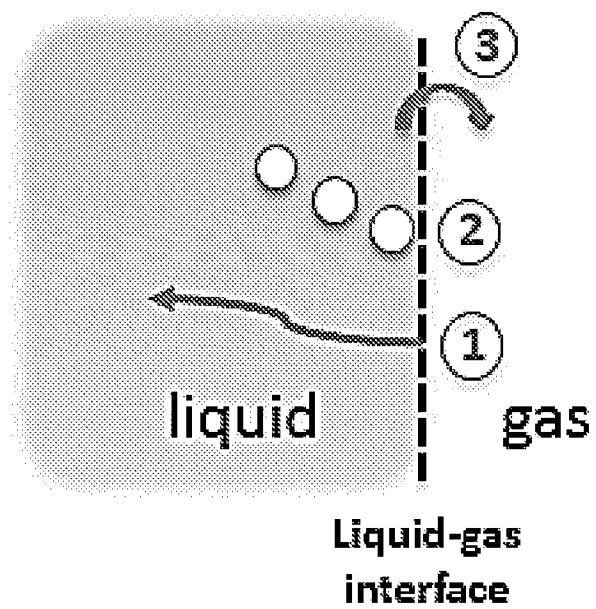
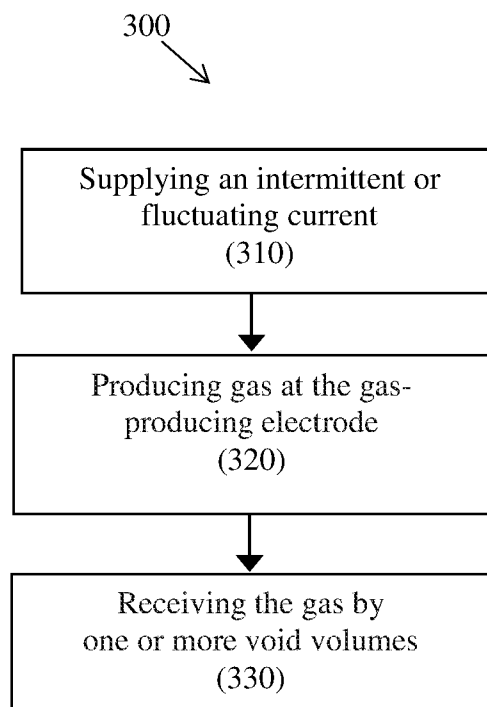


FIGURE 2

**FIGURE 3**

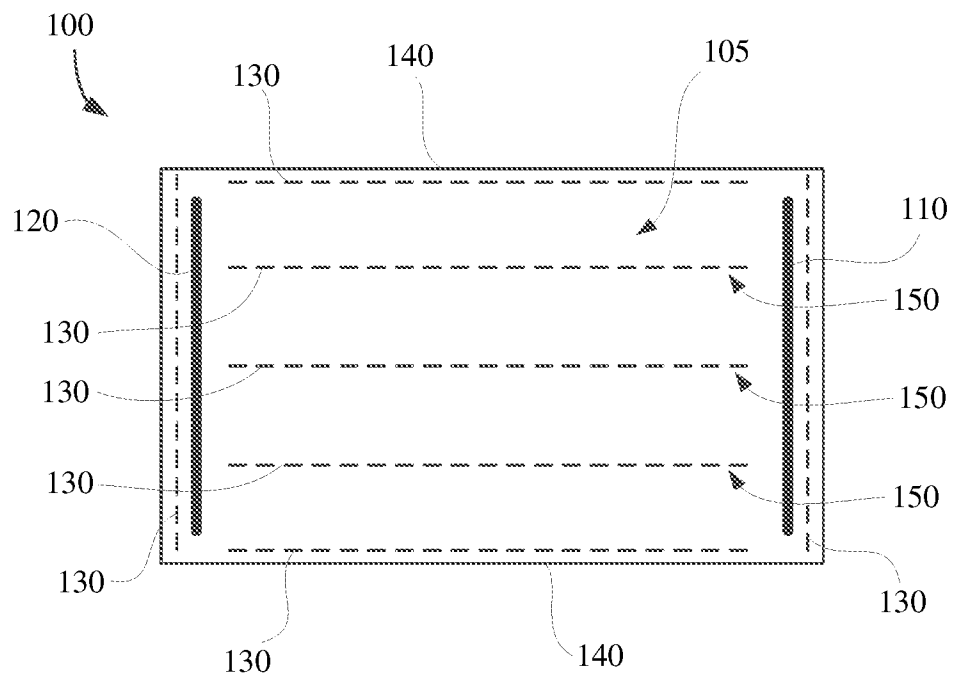


FIGURE 4

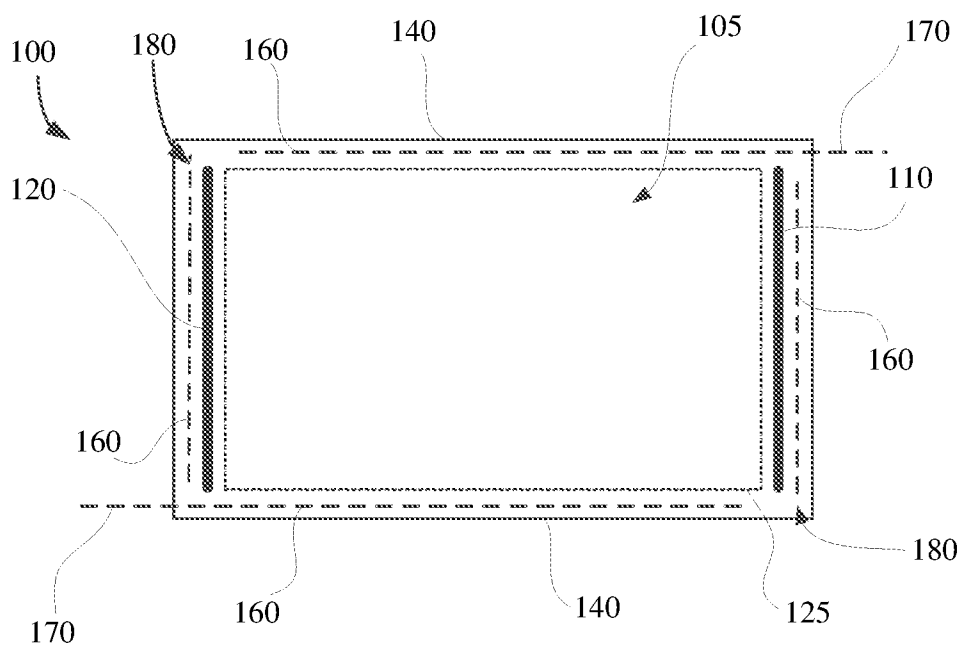


FIGURE 5

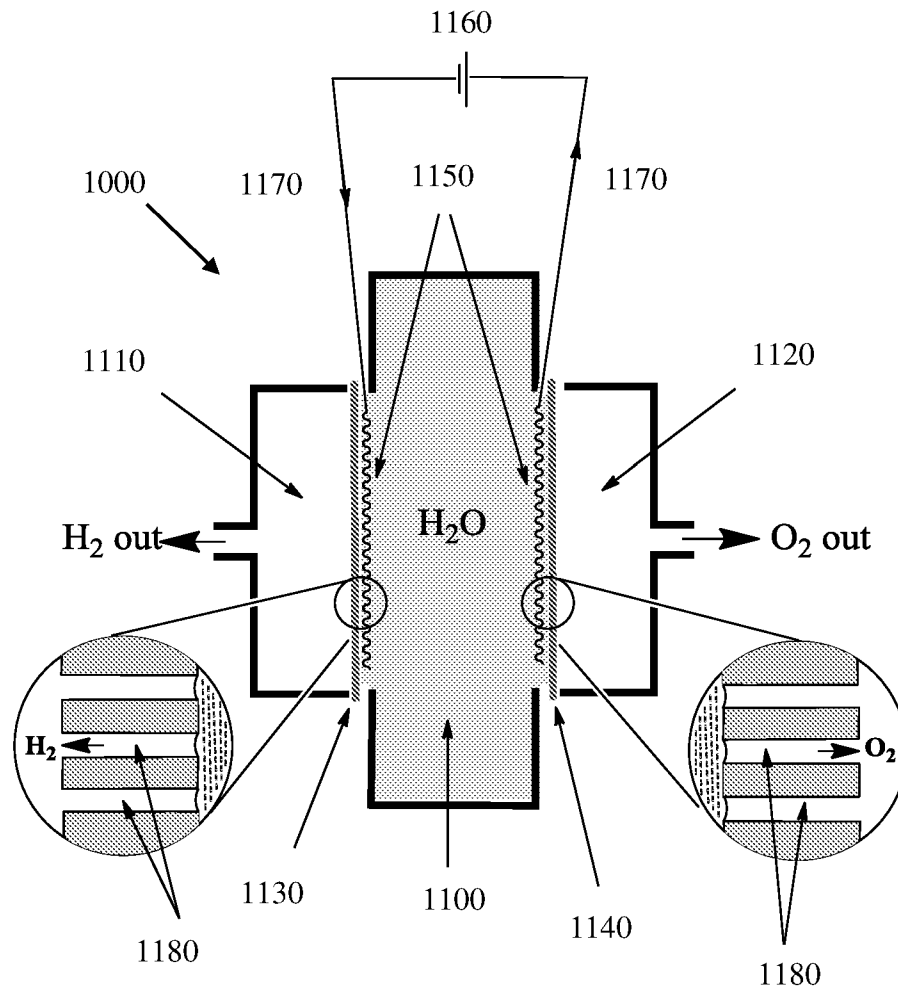
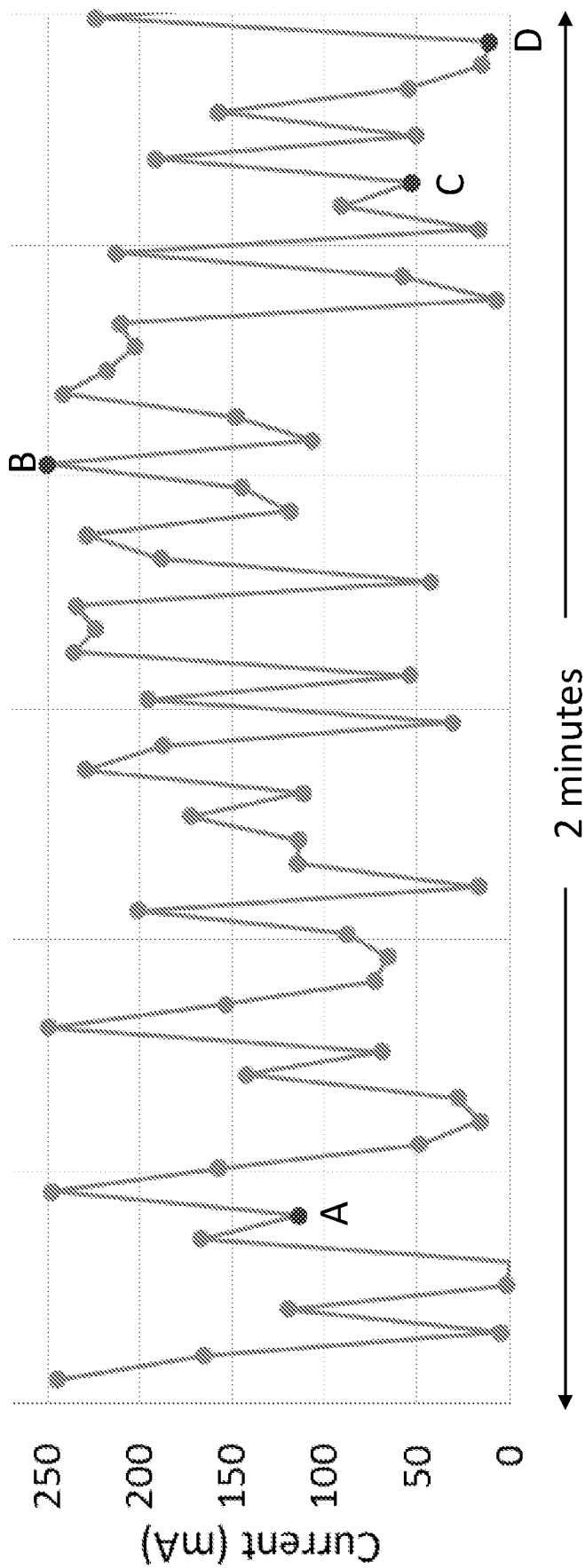


FIGURE 6



Monitored 4 points over time

A: 114.0 mA C: 53.9 mA

B: 249.9 mA D: 10.9 mA

FIGURE 7

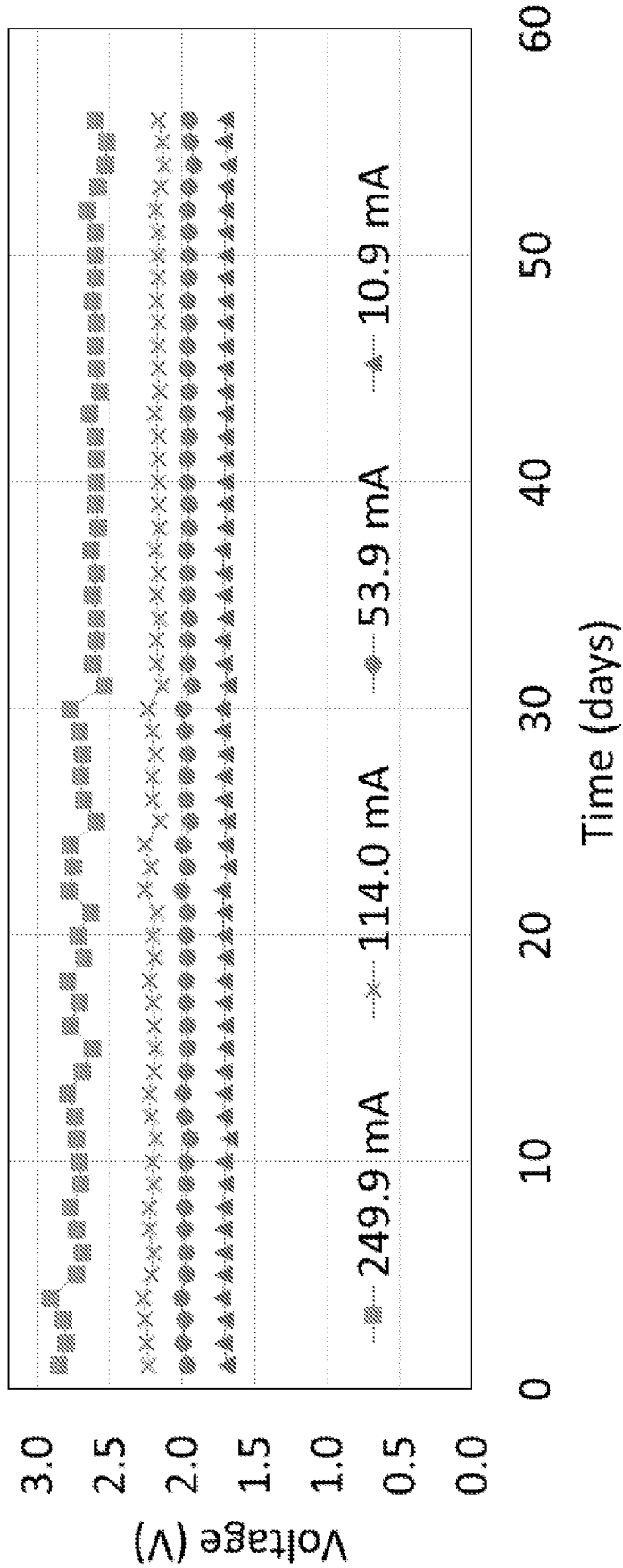


FIGURE 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2016/051230

A. CLASSIFICATION OF SUBJECT MATTER

C25B 11/03 (2006.01) H01M 10/52 (2006.01) C25B 1/04 (2006.01) C25B 1/12 (2006.01) H01M 8/04186 (2016.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

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

Searches were performed in Espacenet, Google Patents, Google Search, Science Direct, EPODOC, WPIAP, TXPEA, TXPEB, TXPEC, TXPEE, TXPEF, TXPEH, TXPEI, TXPEP, TXPEPEA, TXPES, TXPUSE0A, TXPUSE1A, TXPUSEA, TXPUSEB, TXPW0EA. IPC/CPC marks: H01M8/00/LOW, H01M4/00/LOW, H01M10/00/LOW, C25B9/00/LOW, C25B15/00/LOW, C25B1/00/LOW, C25B11/00/LOW, H01M2/00/LOW. Keywords (along with synonyms and proximity operators): Intermittent, liquid, void, porous, bubble, gas, suppress

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 7 February 2017		Date of mailing of the international search report 07 February 2017	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au		Authorised officer Jason Schiemer AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262832810	

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2016/051230
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/0000574 A1 (SUGIMASA ET AL.) 01 January 2009 Figure 1, paragraphs [0020]-[0024], [0037], [0045]-[0046]	1-27, 29-32
X	US 2014/0048423 A1 (SWIEGERS ET AL.) 20 February 2014 Figure 7, paragraphs [0012]-[0014], [0039], [0046]-[0047], [0082], [0146]-[0158]	1-2, 4-12, 15-27, 29-32
X	WO 2013/185170 A1 (UNIVERSITY OF WOLLONGONG) 19 December 2013 Figure 1, paragraphs [020], [024], [054], [077]-[080], [098]-[099], [0153]	1-2, 4, 6-12, 15-27, 29-31

Form PCT/ISA/210 (fifth sheet) (July 2009)

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2016/051230	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
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		JP 2009007647 A	15 Jan 2009
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		AU 2011340809 A1	13 Jun 2013
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End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(July 2009)			