

Device and method for the flexible use of electricity

The present invention relates to a device and a method for flexible use of power, with which excess electrical energy can be utilized for production of hydrogen.

5 The use of renewable energy sources, such as wind energy and solar energy, is gaining ever-increasing significance for the generation of electricity. Electrical energy is typically supplied to a multitude of consumers over long-ranging, supra-regional and transnationally coupled
10 electricity supply networks, referred to as electricity networks for short. Since electrical energy cannot be stored to a significant extent in the electricity network itself, the electrical power fed into the electricity network must be made to match the consumer-side power
15 demand, known as the load. As is known, the load fluctuates time-dependently, in particular according to the time of day, the day of the week or else the time of year. For a stable and reliable electricity supply, a continuous balance of electricity generation and electricity
20 consumption is necessary. Possibly occurring short-term deviations are balanced out by what is known as positive or negative control energy or control power. In the case of regenerative electricity-generating devices, the difficulty arises that, in the case of certain types, such as wind
25 energy and solar energy, the energy-generating capacity is not available at all times and cannot be controlled in a specific way, but is subject to time-of-day and weather-dependent fluctuations, which only under some circumstances are predictable and which generally do not coincide with
30 the energy demand at the particular time.

The difference between the generating capacity of fluctuating renewable energy sources and the consumption at a given time is usually covered by other power plants, such as, for example, gas, coal and nuclear power plants. With
35 fluctuating renewable energy sources being increasingly

extended and covering an increasing share of the electricity supply, ever greater fluctuations between their output and the consumption at the particular time must be balanced out. Thus, even today, not only gas power plants
5 but increasingly also bituminous coal power plants are being operated at part load or shut down entirely in order to balance out the fluctuations. Since this variable operation of the power plants is associated with considerable additional costs, the development of
10 alternative measures has been investigated for some time.

As an alternative or in addition to varying the output of a power plant in the case of an excess of electrical energy, a known approach is to utilize excess electrical energy for production of hydrogen by electrolytic cleavage of water.
15 This approach has the disadvantage that a separate device for electrolytic cleavage of water has to be constructed, which is operated only in the event of an excess of electrical energy and remains unused for most of the time.

The production of chlorine by chlor-alkali electrolysis of a sodium chloride solution is one of the industrial
20 processes with the highest power consumption. For chlor-alkali electrolysis, plants with a relatively large number of electrolysis cells operated in parallel are used in industry. Co-products typically generated in addition to
25 chlorine are sodium hydroxide solution and hydrogen. In order to reduce the power consumption of the chlor-alkali electrolysis, alternative methods have been developed in which there is no reduction of protons to molecular hydrogen at the cathode of the electrolysis cell, but
30 instead reduction of molecular oxygen to water at an oxygen-consuming electrode. The plants known from the prior art for chlor-alkali electrolysis with oxygen-consuming electrodes are not designed for generation of molecular hydrogen.

There have already been proposals, for flexible use of power, to operate a chlor-alkali electrolysis in such a way that a different number of electrolysis cells is operated as a function of the power supply. This approach has the
5 disadvantage that the amount of chlorine produced varies with the power supply and does not correspond to the current demand for chlorine, and so a large buffer reservoir for chlorine becomes necessary for such an operation of a chlor-alkali electrolysis. However,
10 intermediate storage of large amounts of chlorine, a hazardous substance, is undesirable for safety reasons.

It has been found that the disadvantages of the abovementioned devices and methods can be avoided when, in an electrolysis cell for chlor-alkali electrolysis, both an
15 oxygen-consuming electrode as cathode and a second cathode for generation of hydrogen are arranged in the cathode half-cell, and the cathode half-cell is equipped with a conduit for purging of the gas space adjoining the oxygen-consuming electrode, such that the electrolysis cell can be
20 operated, as a function of the power supply, either with generation of hydrogen at the second cathode or with reduction of oxygen at the oxygen-consuming electrode.

The invention provides a device for flexible use of power, comprising an electrolysis cell for chlor-alkali
25 electrolysis having an anode half-cell, a cathode half-cell and a cation exchange membrane that separates the anode half-cell and the cathode half-cell from one another, an anode arranged in the anode half-cell for evolution of chlorine, an oxygen-consuming electrode arranged in the
30 cathode half-cell as the cathode, a catholyte space which is formed between the cation exchange membrane and the oxygen-consuming electrode, and through which electrolyte flows, a gas space adjoining the oxygen-consuming electrode at a surface facing away from the catholyte space, and a
35 conduit for supply of gaseous oxygen to this gas space,

characterized in that a second cathode for generation of hydrogen is arranged within the catholyte space and the device has at least one conduit for purging of the gas space with inert gas.

5 The invention also provides a method for flexible use of power, in which, in an inventive device, chlorine is produced by chlor-alkali electrolysis, wherein when power supply is low, gaseous oxygen is supplied to the oxygen-consuming electrode and oxygen is reduced at the oxygen-
10 consuming electrode at a first cell voltage, and when power supply is high, no oxygen is supplied to the oxygen-consuming electrode and hydrogen is generated at the second cathode at a second cell voltage which is higher than the first cell voltage.

15 The inventive device comprises an electrolysis cell for chlor-alkali electrolysis having an anode half-cell, a cathode half-cell and a cation exchange membrane that separates the anode half-cell and the cathode half-cell from one another. This inventive device may comprise a
20 plurality of such electrolysis cells, which may be connected to form monopolar or bipolar electrolyzers, preference being given to monopolar electrolyzers.

An anode for evolution of chlorine is arranged in the anode half-cell of the inventive device. Anodes used may be any
25 of the anodes known from the prior art for chlor-alkali electrolysis by the membrane method. Preference is given to using dimensionally stable electrodes having a carrier of metallic titanium and a coating with a mixed oxide composed of titanium oxide and ruthenium oxide or iridium oxide.

30 The anode half-cell and cathode half-cell of the inventive device are separated from one another by a cation exchange membrane. Cation exchange membranes used may be any of the cation exchange membranes known to be suitable for chlor-alkali electrolysis by the membrane method. Suitable cation

exchange membranes are available under the Nafion®, Aciplex™ and Flemion™ trade names from Du Pont, Asahi Kasei and Asahi Glass.

An oxygen-consuming electrode is arranged in the cathode half-cell of the inventive device such that the cathode half-cell has a catholyte space, through which electrolyte flows, between the cation exchange membrane and the oxygen-consuming electrode, and a gas space, which can be supplied with oxygen via a conduit for supply of gaseous oxygen, adjoins the oxygen-consuming electrode at a surface facing away from the catholyte space. The device also has at least one conduit for purging of the gas space with an inert gas. The gas space may be continuous over the entire height of the cathode half-cell or may be divided into a plurality of gas pockets arranged vertically one on top of another, in which case the gas pockets each have orifices for pressure equalization with the electrolyte space. Suitable embodiments of such gas pockets are known to those skilled in the art, for example from DE 44 44 114 A1. The conduit for purging of the gas space with an inert gas may be separate from the conduit for supply of gaseous oxygen to the gas space, or it may be connected outside the cathode half-cell to the conduit for supply of gaseous oxygen, such that the conduit section between this connection and the cathode half-cell can be purged with inert gas.

Oxygen-consuming electrodes used may be noble metal-containing gas diffusion electrodes. Preference is given to using silver-containing gas diffusion electrodes, more preferably gas diffusion electrodes having a porous hydrophobic gas diffusion layer containing metallic silver and a hydrophobic polymer. The hydrophobic polymer is preferably a fluorinated polymer, more preferably polytetrafluoroethylene. More preferably, the gas diffusion layer consists essentially of polytetrafluoroethylene-sintered silver particles. The gas diffusion electrode may

additionally comprise a carrier structure in the form of a mesh or grid, which is preferably electrically conductive and more preferably consists of nickel. Particularly suitable multilayer oxygen-consuming electrodes are known
5 from EP 2 397 578 A2. The multilayer oxygen-consuming electrodes known from EP 2 397 578 A2 can be operated with high pressure differentials and can therefore be used in a cathode half-cell with a continuous gas space over the entire height.

10 Furthermore, a second cathode for generation of hydrogen is arranged in the cathode half-cell of the inventive device in the catholyte space. In principle, any of the cathodes known from the prior art for the generation of hydrogen in a chlor-alkali electrolysis may be used as second cathode.
15 The second cathode used is preferably a cathode having a noble metal-containing coating which preferably contains platinum or ruthenium as the noble metal. Preferably, the second cathode is configured in the form of a mesh or grid and directly abuts the cation exchange membrane, such that
20 the electrolyte flows through the catholyte space essentially between the second cathode and the oxygen-consuming cathode.

The oxygen-consuming electrode and the second cathode are preferably electrically insulated from one another in the
25 cathode half-cell and preferably have separate power connections. This allows reliable prevention of formation of hydrogen at the second cathode during the operation of the device with reduction of oxygen at the oxygen-consuming electrode.

30 The inventive device preferably comprises a conduit with which inert gas can be withdrawn from the gas space of the cathode half-cell, and at which there is arranged a sensor which can be used to measure the content of oxygen in the inert gas. The use of such a sensor makes it possible to
35 monitor, whether the gas space has been sufficiently purged

with inert gas to avoid formation of an ignitable gas mixture in the gas space, when changing from operation of the device with reduction of oxygen at the oxygen-consuming electrode to operation with formation of hydrogen at the
5 second cathode.

In a preferred embodiment, the inventive device additionally comprises at least one conduit for purging the catholyte space with inert gas. In this case, the device may comprise a further conduit with which inert gas can be
10 withdrawn from the catholyte space, and this conduit may be connected to a gas collector at the upper end of the catholyte space or may be connected to a separating device which is arranged outside the cathode half-cell and in which gas is separated from electrolyte flowing out of the
15 cathode half-cell. More preferably, the device comprises a conduit with which inert gas can be removed both from the gas space and from the catholyte space of the cathode half-cell, and at which there are arranged one or more sensors with which the content of oxygen and hydrogen in the inert
20 gas can be measured.

The gas space adjoining the oxygen-consuming electrode, any gas pockets present, any gas collector present and the conduits connected to the cathode half-cell for supply and withdrawal of gases are preferably configured such that
25 only low backmixing of gas occurs when purging the gas space and optionally of the catholyte space with inert gas. The gas space, any gas pockets present and any gas collector present are therefore configured with minimum gas volumes.

30 In a preferred embodiment, the inventive device comprises a plurality of electrolyzers arranged in parallel. Each of the electrolyzers then comprises a plurality of electrolysis cells each having a gas space, and a common conduit for supply of gaseous oxygen to the gas spaces of
35 the electrolysis cells of the electrolyser and a common

conduit for purging of the gas spaces of the electrolyser with inert gas. In addition, the device comprises separate conduits for supply of oxygen to the electrolysers and separate conduits for supply of inert gas to the
5 electrolysers. Such a configuration of the device enables, with a low level of apparatus complexity, operation of the device with variability of the proportion of electrolysis cells in which hydrogen is generated.

The inventive device may additionally have a buffer
10 reservoir for chlorine generated in the anode half-cell, which can store an amount of chlorine which can compensate for the interruption in the generation of chlorine in the anode half-cell on purging of the cathode half-cell with inert gas.

15 Fig. 1 shows a preferred embodiment of the inventive device with an electrolysis cell in which the second cathode abuts the cation exchange membrane. The electrolysis cell comprises an anode half-cell (1), a cathode half-cell (2) and a cation exchange membrane (3) that separates the two
20 half-cells. An anode (4) for evolution of chlorine arranged in the anode half-cell abuts the cation exchange membrane. An oxygen-consuming electrode (5) arranged in the cathode half-cell as the cathode divides the cathode half-cell into a catholyte space (6), formed between the cation exchange
25 membrane and the oxygen-consuming electrode, and a gas space (7). The gas space can be supplied with gaseous oxygen via a conduit (8). The gas space can be purged with inert gas via a conduit (10). Inert gas can be withdrawn from the gas space via a conduit (13), and a sensor is
30 arranged at the conduit (13) with which the content of oxygen and hydrogen in the inert gas can be measured. A second cathode (9) for generation of hydrogen, which abuts the cation exchange membrane, is arranged in the catholyte space (6). The oxygen-consuming electrode (5) and the
35 second cathode (9) have separate power connections (11,

12). The catholyte space (6) is supplied with a sodium hydroxide solution via a conduit (15) and an enriched sodium hydroxide solution is withdrawn via a conduit (16), optionally together with hydrogen formed, such that the electrolyte flows through the catholyte space. The catholyte space can be purged with inert gas via a conduit (14). The anode half-cell (1) is supplied with a sodium chloride solution via a conduit (17), and a depleted sodium chloride solution is withdrawn together with chlorine via a conduit (18).

In the inventive method for flexible use of power, chlorine is produced by chlor-alkali electrolysis in a device according to the invention and at least one electrolysis cell in the device is operated with different cell voltages as a function of the power supply. When power supply is low, the oxygen-consuming electrode of the electrolysis cell is supplied with gaseous oxygen, and oxygen is reduced at the oxygen-consuming electrode at a first cell voltage. When power supply is high, the oxygen-consuming electrode is not supplied with oxygen, and hydrogen is generated at the second cathode at a second cell voltage which is higher than the first cell voltage.

Preferably, in the inventive method, the preferred embodiment of the device in which the oxygen-consuming electrode and the second cathode have separate power connections is used, and during operation with the first cell voltage the cell voltage is applied only to the oxygen-consuming electrode, and during operation with the second cell voltage the cell voltage is applied only to the second cathode.

A high power supply may result from a power surplus, and a low power supply may result from a power deficit. A power surplus arises when at some point more power from renewable energy sources is being provided than the total amount of power being consumed at this time. A power surplus also

arises when large amounts of electrical energy are being provided from fluctuating renewable energy sources, and the throttling or shutdown of power plants is associated with high costs. A power deficit arises when comparatively small amounts of renewable energy sources are available and inefficient power plants, or power plants associated with high costs, have to be operated. A power surplus may also exist when the operator of a power generator, for example of a windfarm, is producing more power than has been predicted and sold. Analogously, a power deficit may exist when less power is being produced than predicted. The distinction between a high power supply and a low power supply can alternatively also be made on the basis of a price at a power exchange, in which case a low power price corresponds to a high power supply and a high power price to a low power supply. In this case, for the distinction between a high power supply and a low power supply, it is possible to use a fixed or a time-variable threshold value for the power price at a power exchange.

In a preferred embodiment, a threshold value for a power supply is defined for the inventive method. In that case, the current power supply is determined at regular or irregular intervals and the electrolysis cell is operated with the first cell voltage with supply of gaseous oxygen to the oxygen-consuming electrode when the power supply is below the threshold value, and with the second cell voltage without supply of oxygen to the oxygen-consuming electrode when the power supply is above the threshold value. The threshold value for the power supply and the current power supply can, as described above, be defined or ascertained on the basis of the difference between power generation and power consumption, on the basis of the current output of a power generator, or on the basis of the power price at a power exchange.

By changing between two modes of operation with different cell voltage, it is possible in the inventive method to match the power consumption of the chlor-alkali electrolysis flexibly to the power supply, without any need
5 for alteration of the production output of chlorine and for intermediate storage of chlorine for that purpose. The electrical energy consumed additionally as a result of the higher second cell voltage is used for generation of hydrogen and enables storage of surplus power in the form
10 of chemical energy without the construction and operation of additional installations for power storage. This way, more hydrogen is generated per additional kWh consumed than in the case of hydrogen generation by water electrolysis. Through the use of two different cathodes for the two modes
15 of operation, which can be optimized to the respective mode of operation, it is possible in both modes of operation to work with low overpotentials and to minimize power consumption in the two modes of operation.

Suitable values for the first cell voltage for reduction of oxygen at the oxygen-consuming electrode and for the second
20 cell voltage for production of hydrogen at the second cathode depend on the design of the oxygen-consuming electrode used and of the second cathode, and on the current density envisaged for the chlor-alkali
25 electrolysis, and can be ascertained in a known manner by the measurement of current-voltage curves for the two modes of operation.

The gaseous oxygen can be supplied in the form of essentially pure oxygen or in the form of oxygen-rich gas,
30 in which case the oxygen-rich gas contains preferably more than 50% by volume of oxygen and more preferably more than 80% by volume of oxygen. Preferably, the oxygen-rich gas consists essentially of oxygen and nitrogen, and may optionally additionally contain argon. A suitable oxygen-
35 rich gas can be obtained from air by known methods, for

example by pressure swing adsorption or a membrane separation.

Preferably, when changing from hydrogen generation at the second cell voltage to oxygen reduction at the first cell voltage, the cell voltage is reduced until essentially no more current flows, and the gas space is purged with an inert gas, before gaseous oxygen is supplied to the oxygen-consuming electrode. Analogously and preferably, when changing from oxygen reduction at the first cell voltage to hydrogen generation at the second cell voltage, the cell voltage is reduced until essentially no more current flows, and the gas space is purged with an inert gas, before hydrogen is generated at the second cathode. Suitable inert gases are all gases which do not form ignitable mixtures either with oxygen or with hydrogen and which do not react with aqueous sodium hydroxide solution. The inert gas used is preferably nitrogen. Preferably, purging with inert gas and maintenance of a reduced cell voltage is continued until the content of hydrogen or oxygen in the gas which leaves the cathode half-cell because of the purging falls below a defined limit. The limit for hydrogen is preferably selected such that the mixing of the hydrogen containing gas with pure oxygen cannot give a flammable mixture, and the limit for oxygen is preferably selected such that mixing of the oxygen containing gas with pure hydrogen cannot give a flammable mixture. Suitable limits can be taken from known diagrams for the flammability of gas mixtures, or be ascertained by methods known to those skilled in the art for determining flammability. The reduction in the cell voltage and the purging with inert gas can reliably avoid the formation of flammable gas mixtures when changing between the two modes of operation of the inventive method.

When changing from hydrogen generation at the second cell voltage to oxygen reduction at the first cell voltage, the

purging with inert gas is preferably additionally followed by purging with an oxygen containing gas, in order to avoid mass transfer inhibition in the reduction of oxygen as a result of a high content of inert gas in the gas diffusion layer of the oxygen-consuming electrode.

Preferably, a prediction of the expected power supply is made for the method of the invention, a minimum duration for operation with the first and with the second cell voltage is set, and a swichover between operation with the first cell voltage with supply of gaseous oxygen to operation with the second cell voltage without supply of oxygen is performed only when the predicted duration of a low or high power supply is longer than the minimum duration set. Through such a mode of operation, it is possible to avoid losses of production capacity for chlorine as a result of too many changes of the cell voltage and associated interruptions in chlorine production during purging with inert gas.

In a preferred embodiment of the inventive method, after changing from oxygen reduction at the first cell voltage to hydrogen generation at the second cell voltage, a gas mixture comprising hydrogen and inert gas is withdrawn from the cathode half-cell and hydrogen is separated from this gas mixture, preferably through a membrane. With such a separation, essentially all the hydrogen generated can be obtained in high purity and with constant quality.

Preferably, the method of the invention is performed in a device having a plurality of electrolysis cells according to the invention, and the proportion of electrolysis cells to which no oxygen is supplied and in which hydrogen is generated at the second cathode is altered as a function of the power supply. More preferably, for this purpose, the device described above with a plurality of electrolyzers arranged in parallel is used, and the proportion of the electrolyzers to which no oxygen is supplied and in which

hydrogen is generated at the second cathode is altered as a function of the power supply. This allows for adjusting the power consumption of the chlor-alkali electrolysis within a wide range with essentially constant chlorine production.

- 5 In this embodiment, the inventive method can be used, without any adverse effects on chlorine production, for providing negative control energy for the operation of a power distribution grid.

Claims:

1. Device for flexible use of power, comprising an electrolysis cell for chlor-alkali electrolysis having an anode half-cell, a cathode half-cell and a cation exchange membrane that separates the anode half-cell and the cathode half-cell from one another, an anode arranged in the anode half-cell for evolution of chlorine, an oxygen-consuming electrode arranged in the cathode half-cell as the cathode, a catholyte space which is formed between the cation exchange membrane and the oxygen-consuming electrode, and through which electrolyte flows, a gas space adjoining the oxygen-consuming electrode at a surface facing away from the catholyte space, and a conduit for supply of gaseous oxygen to this gas space, characterized in that a second cathode for generation of hydrogen is arranged within the catholyte space and the device has at least one conduit for purging of the gas space with inert gas.
2. Device according to Claim 1, characterized in that the oxygen-consuming electrode and the second cathode have separate power connections.
3. Device according to Claim 1 or 2, characterized in that it comprises a conduit with which inert gas can be withdrawn from the gas space, and at this conduit a sensor is arranged with which the content of oxygen in the inert gas can be measured.
4. Device according to any one of Claims 1 to 3, characterized in that it additionally comprises at least one conduit for purging the catholyte space with inert gas.
5. Device according to any one of Claims 1 to 4, characterized in that the second cathode abuts the cation exchange membrane.

6. Device according to any one of Claims 1 to 5,
characterized in that the oxygen-consuming electrode has
a porous hydrophobic gas diffusion layer containing
metallic silver and a fluorinated polymer.

5 7. Device according to any one of Claims 1 to 6,
characterized in that it comprises a plurality of
electrolysers arranged in parallel, each of the
electrolysers comprising a plurality of electrolysis
10 cells each having a gas space, and a common conduit for
supply of gaseous oxygen to the gas spaces of the
electrolysis cells of the electrolyser and a common
conduit for purging of the gas spaces of the
electrolysis cells of the electrolyser with inert gas,
and the device comprises separate conduits for supply of
15 oxygen to the electrolysers and separate conduits for
supply of inert gas to the electrolysers.

8. Method for flexible use of power, characterized in that,
in a device according to any one of Claims 1 to 7,
chlorine is produced by chlor-alkali electrolysis,
20 wherein

a) when power supply is low, the oxygen-consuming
electrode is supplied with gaseous oxygen, and oxygen
is reduced at the oxygen-consuming electrode at a
first cell voltage, and

25 b) when power supply is high, the oxygen-consuming
electrode is not supplied with oxygen, and hydrogen
is generated at the second cathode at a second cell
voltage which is higher than the first cell voltage.

9. Method according to Claim 8, characterized in that, when
30 changing from hydrogen generation at the second cell
voltage to oxygen reduction at the first cell voltage,
the cell voltage is reduced until essentially no current
flows, and the gas space is purged with an inert gas,

before gaseous oxygen is supplied to the oxygen-consuming electrode.

10. Method according to Claim 8 or 9, characterized in that, when changing from oxygen reduction at the first cell voltage to hydrogen generation at the second cell voltage, the cell voltage is reduced until essentially no current flows, and the gas space is purged with an inert gas, before hydrogen is generated at the second cathode.
11. Method according to any one of Claims 8 to 10, comprising the steps of
- a) defining a threshold value for a power supply,
 - b) determining the power supply,
 - c) operating the electrolysis cell with the first cell voltage with supply of gaseous oxygen to the oxygen-consuming electrode when the power supply is below the threshold value and operating the electrolysis cell with the second cell voltage without supply of oxygen to the oxygen-consuming electrode when the power supply is above the threshold value, and
 - d) repeating steps b) and c).
12. Method according to any one of Claims 8 to 11, characterized in that nitrogen is used as the inert gas.
13. Method according to any one of Claims 8 to 12, characterized in that, after a swichover from oxygen reduction at the first cell voltage to hydrogen generation at the second cell voltage, a gas mixture comprising hydrogen and inert gas is withdrawn from the cathode half-cell and hydrogen is separated from this gas mixture through a membrane.

14. Method according to any one of Claims 8 to 13,
characterized in that the device has a plurality of
electrolysis cells according to any one of Claims 1 to
6, and the proportion of the electrolysis cells to which
5 no oxygen is supplied and in which hydrogen is generated
at the second cathode is altered as a function of the
power supply.
15. Method according to any one of Claims 8 to 14,
characterized in that a prediction of the expected power
10 supply is made, a minimum duration for operation with
the first and with the second cell voltage is set, and a
switchover between operation with the first cell voltage
with supply of gaseous oxygen to operation with the
second cell voltage without supply of oxygen is
15 performed only when the predicted duration of a low or
high power supply is longer than the minimum duration
set.