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ELECTROLYTIC PRODUCTION OF HYDROGEN AND OXYGEN

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This invention relates to the electrolysis of water for the production of hydrogen and oxygen using an aqueous caustic alkali electrolyte in an electrolytic cell, and is particularly directed to providing an addition agent which has the property of substantially reducing the operating voltage normally required for effecting such electrolysis.

This application is a continuation-in-part of abandoned co-pending application Serial No. 399,932, filed June 26, 1941.

The decomposition of water for the commercial production of hydrogen and oxygen involves the use of an electrolytic cell and an electrolyte formed, usually, of an aqueous caustic alkali solution in which the caustic alkali, such as sodium hydroxide or potassium hydroxide, is present to increase the electrical conductivity of the electrolyte.

In general, the electrolytic cells, which are of the tank or filter-press type, use mild steel or iron cathodes and nickel plated iron anodes. The design of the cell and its associated parts is preferably such that contact voltages are reduced to a minimum.

In the operation of an electrolytic cell, it is desirable that the voltage between the electrodes be maintained as low as reasonably possible in order to operate the cell with a low consumption of power to obtain the highest possible power efficiency consistent with other considerations of economy.

The addition agent of the present invention comprises, in general, a substance which is soluble in an aqueous, caustic alkali electrolyte and of which each molecule contains at least one vanadium atom as an essential constituent. It has been found that the introduction of such an addition agent into an aqueous caustic alkali electrolyte used for the production of hydrogen and oxygen, even in small amounts, has the effect of lowering the normal operating voltage of the cell.

It has been found also that the presence of such impurities as zinc, lead, tin, germanium or thallium, even in small concentrations in the caustic alkali electrolyte, frequently results in an increase in the voltage which must be supplied to operate the cell, thus lowering the power efficiency and increasing the cost of operating the cell.

As a specific example of the effects of the presence of zinc, a cell was operated at a current density of about 67 amperes per square foot of cathode surface and the zinc depositing on the cathodes caused an increase in the voltage be-

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tween the electrodes of 0.30 volt, from the original 2.28 volts to 2.58 volts.

It has been found that the treatment of the electrolyte with the present addition agent causes a substantial lowering of the operating voltage. It has been found also that the reduction in the operating voltage is such that a rise in voltage, if any, due to the presence of impurities such as those cited previously, is counteracted. While the invention is entirely independent of theoretical considerations as to the manner in which these results are produced by the addition agent, a possible explanation may be that vanadium atoms, contained in the addition agent, are deposited, probably combined for the most part with atoms of at least one other element, as a film on the cathodes, with the result that the cathode surfaces present a lower over-voltage with respect to hydrogen when coated with the film than when no such film is present. This explanation may also apply to the voltage reduction obtained when impurities are present in the electrolyte, as the deposit containing vanadium atoms may partially or completely cover the deposited impurities with the result that the undesirable effect of the impurities is partially or completely counteracted.

The addition agent contains vanadium atoms and is such that on being dissolved in the electrolyte, vanadium atoms are obtained in solution therein. The vanadium atoms may be introduced into the electrolyte by dissolution therein of elemental vanadium, such as by anodic dissolution of ferro-vanadium alloy therein, or they may be added in the form of a vanadium compound which is soluble in the caustic alkali electrolyte. For example, the addition agent may be added directly to the electrolyte as vanadium pentoxide or as a vanadate, such as sodium or potassium metavanadate, or in the form of salts of vanadium, such as the chloride or the sulphate, with consequent improvement in the operating voltage. The vanadium is preferably in the form of a compound which may be dissolved conveniently in caustic alkali electrolyte to form a solution which may then be added to the electrolyte in the cell.

The following examples serve to illustrate the improved operating results obtained by the use of the addition agent of the present invention.

Example 1.—In a laboratory test, a cell, operated with a 25% caustic potash solution as electrolyte and at a temperature of about 70° C., showed an initial operating voltage of 1.98 volts. The addition of 100 mg. of zinc per litre to the electrolyte raised the operating voltage to 2.31 volts. At this point, it was found that the addi-

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tion of vanadium in the form of vanadium pentoxide to the extent of about 500 mg. V_2O_5 per litre of electrolyte lowered the voltage to 1.93 volts. After the vanadium addition, further additions of zinc up to a total of 200 mg. per litre of electrolyte did not raise the voltage above 1.93 volts.

Example 2.—In a test on a commercial scale, using a cell of 10,000 ampere design, containing 25% caustic potash solution as electrolyte, operated at a current density of 67 amperes per square foot and at a temperature of about 70° C., and containing about 200 mg. of zinc per litre of electrolyte as impurity, the voltage was 2.28 volts. The addition to the electrolyte of one pound of vanadium pentoxide (corresponding to an initial concentration of about 300 mg. of vanadium per litre of electrolyte) reduced the voltage to about 2.10 volts.

The following examples, 3, 4, 5 and 6, are illustrative of the effect of the addition agent where either tin, lead, thallium or germanium is present as an impurity. In these tests laboratory cells were used, operating with a 25% caustic potash solution as electrolyte, at a current density of 65 amperes per square foot and at a temperature of 70° C.

Example 3.—The addition of 100 mg. of tin per litre of electrolyte raised the operating voltage of a cell from 2.13 to 2.43 volts. About 300 mg. of vanadium in the form of vanadium pentoxide was then added per litre of electrolyte and the operating voltage dropped to its original value of 2.13 volts.

Example 4.—The addition of 50 mg. of lead per litre of electrolyte raised the operating voltage of a cell from 2.02 to 2.34 volts. About 300 mg. of vanadium in the form of vanadium pentoxide was then added per litre of electrolyte and the operating voltage dropped to 2.03 volts.

Example 5.—The addition of thallium to a cell electrolyte raised the operating voltage from 2.08 to 2.11 volts. About 300 mg. of vanadium in the form of vanadium pentoxide was then added per litre of electrolyte and the operating voltage dropped to 2.05 volts.

Example 6.—The addition of germanium to a cell electrolyte raised the operating voltage from 2.03 to 2.11 volts. About 300 mg. of vanadium in the form of vanadium pentoxide was then added per litre of electrolyte and the operating voltage dropped to its original value of 2.03 volts.

It will be observed that the results obtained in the above four tests, Examples 3, 4, 5 and 6, are similar to those obtained when zinc is present as an impurity in the electrolyte.

Example 7.—In a laboratory test cell containing an electrolyte comprising a 25% solution of laboratory reagent grade caustic potash, operated at a current density of 65 amperes per square foot and at a temperature of 70° C., the addition of 300 mg. of vanadium in the form of vanadium pentoxide per litre of electrolyte lowered the voltage 0.05 volt.

Example 8.—In a test on a group of cells of 10,000 ampere design, each cell containing a 25% solution of high purity technical grade caustic potash as electrolyte, operated at a current density of 67 amperes per square foot and at a temperature of about 70° C. and where every possible precaution was taken to prevent contamination by impurities, the addition to each cell of about 300 mg. of vanadium, in the form of vanadium pentoxide, per litre of electrolyte, lowered the average operating voltage from 2.24 to 2.08 volts.

It will be observed from Examples 7 and 8 that

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a substantial reduction in voltage is obtained by the application of the addition agent of the present invention when high purity electrolyte is used which contains, at the most, only very small quantities of impurities.

In the large scale, commercial production of hydrogen and oxygen, where commercial grade electrolyte is used, the effect of the addition agent in lowering the operating voltage is recognizable and measurable even when only minute amounts of addition agent are added to the electrolyte, for example, amounts equivalent stoichiometrically to about 3 mg. of vanadium per litre of electrolyte. It is difficult to determine the effect of amounts of addition agent equivalent to less than 3 mg. of vanadium per litre due to the normal fluctuations in the cell voltage. Larger initial amounts of addition agent added to the electrolyte produce correspondingly greater reductions in voltage, up to amounts that provide concentrations equivalent to about 300 mg. of vanadium per litre. A slightly greater reduction in operating voltage may be obtained with quantities of addition agent that provide more than 300 mg. per litre, but the increase in voltage reduction under any prescribed set of operating conditions appears to approach a limit beyond which the addition of further amounts of addition agent does not cause any appreciable further reduction in voltage. For example, additions of vanadium pentoxide to the electrolyte in amounts corresponding to about 10 grams of vanadium per litre have been found to contribute only a slight improvement over the addition of vanadium pentoxide in amounts corresponding to about 300 mg. of vanadium per litre in cells operating at normal voltages under similar conditions. The extent of the reduction in operating voltage depends not only on the amount of addition agent added to the electrolyte but also on several other factors, such as, for example, the operating voltage before treatment, the type of impurities that may be present in the electrolyte, and the concentration of such impurities in the electrolyte. The optimum amount of addition agent to be added to the electrolyte can be determined readily by experiment, for example, different amounts of addition agent may be added to different cells and the operating voltage across each cell measured after a few days' operation. In large scale processes for the electrolytic production of hydrogen and oxygen, it is preferred to maintain in the cell electrolyte the concentration of addition agent provided by adding to the untreated electrolyte vanadium in the form of vanadium pentoxide in the order of from about 100 mg. to 1000 mg. and preferably about 500 mg. V_2O_5 per litre. It is preferred to use vanadium pentoxide as it is the commercial product that most economically provides vanadium atoms in a form suitable for convenient addition to the electrolyte.

Commercial grade fused vanadium pentoxide powder, containing about 85% V_2O_5 , has been found to be satisfactory for use as the addition agent. The chemical analysis of commercial grade V_2O_5 is, for example, as follows:

H ₂ O	SiO ₂	Al ₂ O ₃ , Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	V ₂ O ₅	CaO
Per Cent 1.0	Tr	Per Cent 1.7	Tr	Per Cent 5.8	Per Cent 4.8	Per Cent 84.0	Tr

The vanadium pentoxide powder can easily be

added to the electrolytic cells in controlled amounts by dissolving a measured quantity of the powder in an aqueous caustic alkali solution, such as the cell electrolyte. After the powder has been dissolved and the resultant solution is added to the electrolyte in a cell, it will be found that the operating voltage of the cell is reduced compared with the operating voltage obtaining before the addition agent was added to the electrolyte.

It has been indicated hereinbefore that it is believed that the voltage reduction is caused, at least in part, by the formation on the cathodes of a film containing vanadium atoms, this film being deposited on the cathode surfaces during operation of the cell. Continuous operation of the cells for a period of several months after dissolving the addition agent in the electrolyte may result in a gradual decrease of the initial voltage reduction. This decrease in voltage reduction may be caused by the deposition of impurities on the cathode film that contains vanadium atoms, or loss of this film from the cathodes. It has been found that the gradual decrease in the effect of the initial treatment with the addition agent can be overcome by supplementary treatment, in the previously described manner, with further amounts of the addition agent. Extended operation of the process on a commercial scale may be illustrated by reference to Example 8. After a period of several months it may be found that the voltage reduction initially produced by adding about 500 mg. V_2O_5 per litre of electrolyte has appreciably decreased. To ensure a reduction in voltage throughout the operating period of the cell, supplementary treatments with the addition agent, corresponding to about 125 mg. V_2O_5 per litre of electrolyte, may be employed as required, for example, at intervals of 3 to 4 months. These supplementary treatments may be made at more frequent intervals using smaller quantities of addition agent, if desired, or the treatment may be made continuous after the initial addition by supplying very small amounts of a solution of the addition agent daily to the feed water of the cell.

Analyses of the deposits on the cathodes of cells that have been treated with the addition agent reveal the presence, in the deposit, of the elements silicon, aluminum, magnesium, calcium, iron, vanadium, carbon, and oxygen. The silicon, aluminum, magnesium, and calcium appear to occur in the deposits as oxides, and probably come from other parts of the cell, for example, the asbestos diaphragms that surround the electrodes and that are usually employed in commercial cells for the production of hydrogen and oxygen. The presence of iron in the deposit is accounted for in the use of steel tanks to contain the electrolyte, and of iron or steel electrodes. Vanadium, of course, is added to the cell in accordance with the present invention. Carbon is present in the deposit as carbonate, formed in the electrolyte by carbonation of the caustic alkali solution with atmospheric carbon dioxide. The oxygen is combined in the form of oxides and salts. Deposits containing the above mentioned elements other than vanadium also occur on the cathodes of cells that have not been treated with the addition agent, but such deposits do not effect a reduction in the operating voltage of the cells.

The complex chemical nature of vanadium is well known, and because of this complexity, the effective form in which the vanadium atoms occur on the cathodes in cells treated in accordance with the invention has not been determined.

When vanadium in the form of vanadium pentoxide is dissolved in the electrolyte, and the cell has operated for a time, it has been found that the cathode film contains vanadates and vanadium oxides, but other molecular and ionic forms of vanadium may also be present. Although the cathode film, containing vanadium atoms, is known to be responsible for at least part of the voltage reduction, it may be that vanadium atoms in the electrolyte or at the anode also exert some effect. However, in view of the simplicity of the process, the complicated chemical and ionic reactions that may occur with vanadium atoms in caustic alkali electrolyte undergoing electrolysis are not of primary interest. The important fact in connection with the invention is that a reduction in operating voltage is obtained when vanadium atoms are included in the caustic alkali electrolyte.

It has been found, also, that the use of the addition agent in the electrolyte has the further advantage of removing at least one of the causes of the production of mixed hydrogen and oxygen gases at the anodes when the cell is being depolarized. For example, if the electrolyte contains zinc as an impurity, a considerable portion of the zinc present may be deposited on the cathodes during the operation of the cell. When the cells are standing idle, the zinc deposited on the cathodes gradually redissolves with the formation of hydrogen at the cathodes. However, if a battery of cells is depolarized by electrically connecting the terminals, the dissolution takes place more rapidly and the hydrogen evolution partly or entirely occurs at the anodes. The hydrogen produced at the anodes mixes with the oxygen that may be present in the collecting system or with the oxygen produced when the cell is again put into productive operation. The gas recovered from the anodes during the first few minutes of operation after depolarization may thus be potentially explosive. Other metallic impurities, for example tin, which has electrochemical properties comparable to those of zinc, show a similar effect.

While the use of the addition agent in the electrolyte, presumably by its corrective action on the impurities in the electrolyte or the impurities deposited on the cathodes, has been found to remove one of the sources of the production of mixed hydrogen and oxygen gas at the anode when the cell is being depolarized, it must be understood that other factors besides the presence of impurities may also cause a mixed hydrogen-oxygen gas at the anode when starting the operation of a cell after depolarization, so that the use of the addition agent does not ensure the elimination of this hazard.

It has been found in the commercial production of hydrogen and oxygen, that the inclusion of the addition agent in the caustic alkali electrolyte by dissolution therein has resulted in a substantial reduction in the voltage necessary to maintain a predetermined current density in the cells. This reduction in voltage effects a reduction in power consumption with a considerable saving in the cost of producing hydrogen and oxygen or, alternatively, by reason of the voltage reduction due to the prescribed treatments, additional cells can be operated to increase the total output of hydrogen and oxygen, without increasing power consumption. In the actual practice of the invention by the latter alternative, it has been found possible to increase the output of

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hydrogen and oxygen by about 5% without any increase in power consumption.

It will be clearly understood that the practice of the invention is not limited to the specific examples set out hereinabove. Further modifications may become apparent to those skilled in the art in the light of the teachings herein without departing from the scope of the invention as defined by the appended claims.

What we claim as new and desire to protect by Letters Patent of the United States is:

1. A process for the production of hydrogen and oxygen which comprises electrolyzing an aqueous caustic alkali electrolyte containing a vanadium containing substance in solution within the range equivalent to from 3 mg. of vanadium to 10,000 mg. per litre of electrolyte, the quantity of vanadium containing substance in the electrolyte being sufficient to maintain a film containing vanadium on the cathodes.

2. A process for the production of hydrogen and oxygen by the electrolysis of an aqueous caustic alkali electrolyte which includes the step of adding a vanadium containing substance to the electrolyte in a form in which it is soluble in the electrolyte and in amount sufficient to maintain a concentration of vanadium containing substance in the electrolyte equivalent to the range of from 3 mg. to 10,000 mg. of vanadium per litre of electrolyte.

3. A process for the production of hydrogen and oxygen by the electrolysis of an aqueous caustic alkali electrolyte which includes the step of adding vanadium pentoxide to the electrolyte in amount sufficient to maintain a concentration of vanadium in the electrolyte within the range of from 3 mg. to 10,000 mg. of vanadium per litre of electrolyte.

4. A process for the production of hydrogen and oxygen by the electrolysis of an aqueous

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caustic alkali electrolyte which includes the step of adding a vanadium containing substance to the electrolyte in a form in which it is soluble in the electrolyte and in amount sufficient to maintain a concentration of vanadium containing substance in the electrolyte equivalent to the range of from 100 to 1,000 mg. of vanadium pentoxide per litre of electrolyte.

5. A process for the production of hydrogen and oxygen by the electrolysis of an aqueous caustic alkali electrolyte which includes the step of adding vanadium pentoxide to the electrolyte in amount sufficient to maintain a concentration of vanadium containing substance in the electrolyte equivalent to the range of from 100 mg. to 1,000 mg. of vanadium pentoxide per litre of electrolyte.

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