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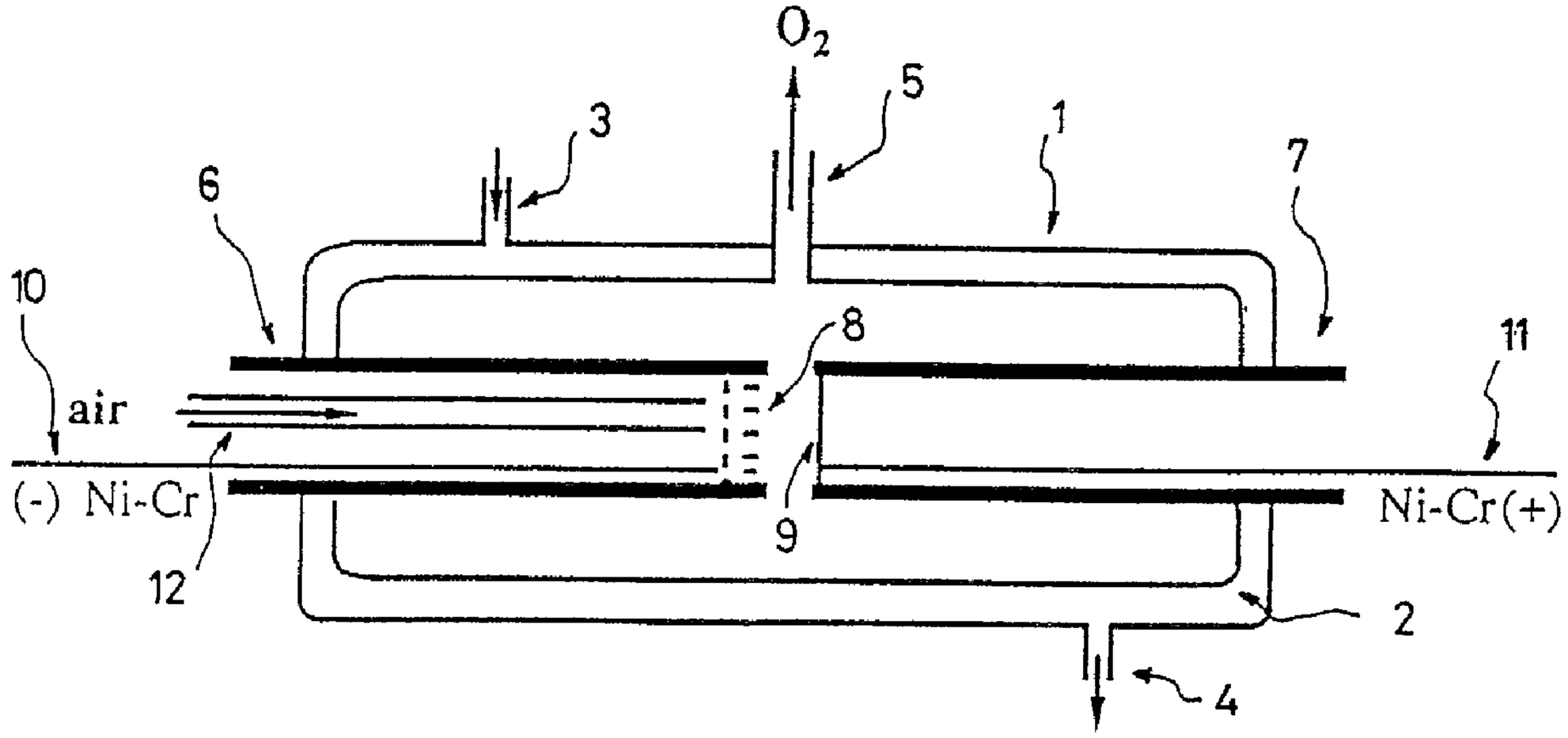

(57) Abrégé/Abstract:
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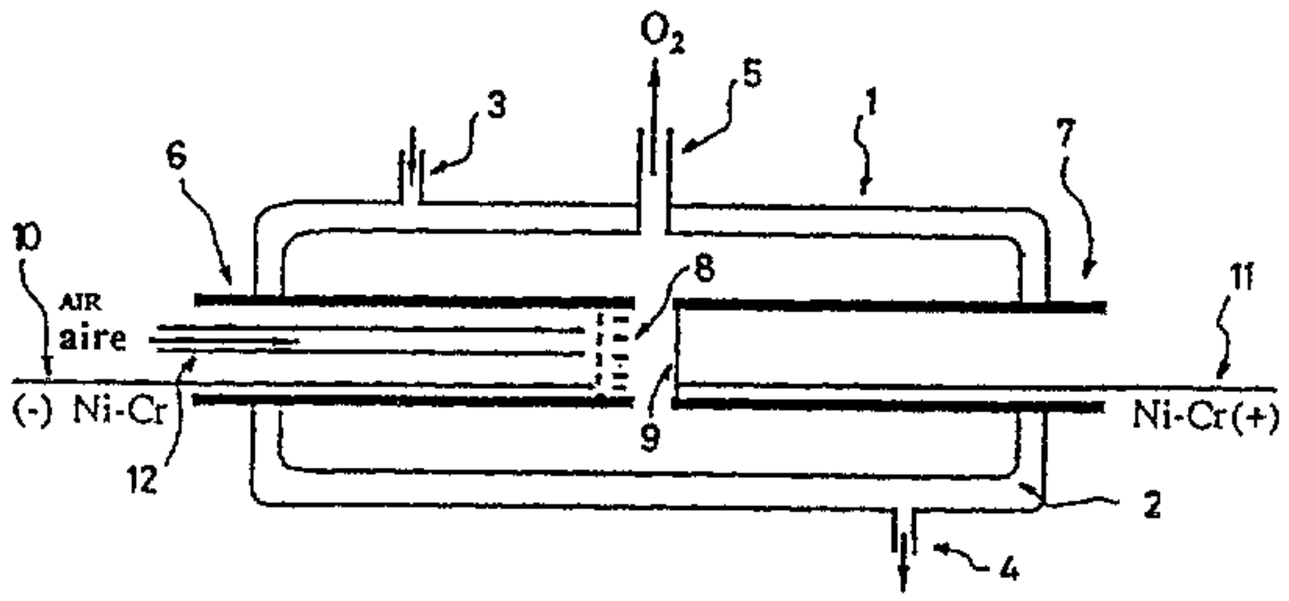
(54) Title: PROCESS FOR THE ELECTROLYTIC SEPARATION OF OXYGEN FROM ITS MIXTURES AND EQUIPMENT FOR IMPLEMENTING SUCH PROCESS

(54) Título: PROCEDIMIENTO PARA LA SEPARACION ELECTROLITICA DEL OXIGENO DE SUS MEZCLAS Y EQUIPO PARA LA REALIZACION DE ESTE PROCEDIMIENTO



(57) Abstract

he process comprises the following steps: a) bringing into contact an oxygen containing gas with a gas diffusion cathode which does not contain a hydrogen peroxyde decomposition catalyst, b) providing a potential difference between the cathode and an anode, so that the oxygen is converted to peroxyde at the cathode, the peroxyde is diffused through an aqueous electrolyte up to the anode, and the peroxyde is converted to pure oxygen at the anode, the process is a new method capable of separating the oxygen through a bi-electronic process. The equipment comprises a single compartment electrolytic cell (1) with at least one cathode (8) and one anode (9), an inlet (12) through the cathode for the introduction of a gas mixture which contains oxygen and an outlet (5) for pure oxygen produced in the cell.

A PROCESS FOR THE ELECTROLYTIC SEPARATION OF OXYGEN FROM ITS MIXTURES AND EQUIPMENT TO PERFORM THIS PROCESS

The present invention relates to an electrochemical process for separation and purification of oxygen from gas mixtures containing it (e.g. air) in an aqueous medium. The invention also relates to the equipment used to perform this process.

BACKGROUND OF THE INVENTION

The present invention is restricted to the use of aqueous electrolytes, and therefore references to organic electrolytes (e.g. dimethylsulphoxide + tetraalkylammonium tetrafluoroborate) or to solid ionic conductors (e.g. yttrium oxide-stabilized zirconium oxide) which have also been used for the obtention or purification of oxygen are not included herein.

Thus, for instance, processes for concentrating oxygen from a feed gas containing it by using solid electrolytes that comprise ion-exchange resins are well known and have been described, e.g. in US Patent US-5,338,412. However, such processes do not allow the obtention of pure oxygen since the electrolyte used exhibits permeability not only to oxygen gas but also to other gases such as nitrogen gas. This permits only to concentrate oxygen but not the obtention of pure oxygen from a gas mixture containing it. On the other hand, systems employed for said concentration of oxygen comprise two electrodes spaced apart by a solid polymer with an ion-exchange resin, so that when the conductivity of said polymer decreases, the whole system must be replaced due to the fact that the polymer and the electrodes form a single compact unit, thereby involving an additional cost to the system.

Likewise, systems for separating oxygen based in Fe- or Co- organometallic complexes, which may act as carriers to facilitate the transport of said gas in a similar manner as haemoglobin does in blood, are also explicitly excluded from this invention. When referring to the prior art we have limited ourselves to those publications closer to the subject invention.

In recent years, many papers relative to cathodic reduction of oxygen on graphite and gas-diffusion electrodes in different aqueous media have been published. Gas-diffusion electrodes are essentially constituted of carbon powders (carbon black) mixed with polytetrafluoroethylene (PTFE) as a binder, which are hot-pressed on a support (normally a metal mesh) that also acts as a current distributor. Under these conditions, the electroreduction process of oxygen is bielectronic and leads to formation of either hydrogen peroxide at pH<11,6 or its conjugated base, hydroperoxide ion, at pH>11,6. The reactions taking place in this process are the following [Yeager E., Electrochim. Acta, 29, 1572 (1984):

pH<5 $$O_2 + 2\ H^+ + 2\ e^- \longrightarrow H_2O_2 \qquad (1a)$$

5<pH<11.6 $$O_2 + 2\ H_2O + 2\ e^- \longrightarrow H_2O_2 + 2\ OH^- \qquad (1b)$$

pH>11.6 $$O_2 + H_2O + 2\ e^- \longrightarrow HO_2^- + OH^- \qquad (1c)$$

The first electrochemical synthesis of hydrogen peroxide by reduction of oxygen is due to Traube and dates back to 1882. This reaction has been studied in acidic and basic media, and even in pure water with a proton-exchange membrane of Nafion® 117 as the electrolyte [Tatapudi P. and J.M. Fenton, J. Electrochem. Soc., 140, L55 (1993). The best current-efficiencies for generation of H_2O_2 have been

obtained in a basic medium. Thus, Mathur, James and Bisset [European Patent No. 248433 (1987); US Patent No. 4,927,509 (1990)] have used a bipolar cell with a permeable diaphragm Celgard®, an oxygen-fed graphite-carbon-PTFE cathode and a Ni anode with an electrocatalytic amount of Co- and W-compounds to produce HO_2^- (30.5 g/l) in a NaOH-containing aqueous solution (38.5 g/l). The current-efficiency was 92.2% for a current-density (j) of 0.3 A/square inch and a voltage (V) of 1.78 V. Moreover, Do and Chen [J. Electrochem. Soc., 140, 1632 (1993)] have studied the effect of pH and temperature on electrogeneration of H_2O_2 in the cathodic compartment of a H-type cell by using O_2-fed graphite as a cathode, and a Pt wire as an anode. These authors have found an efficiency of 88.4% upon circulation of a current-density of 50 mA cm^{-2} at pH = 13 and 25°C, and they consider that the loss of electrogenerated hydroperoxide-ions is due to the following decomposition reaction in a basic medium:

$$2\ HO_2^- \longrightarrow O_2 + 2\ OH^- \qquad (2)$$

The most common method for electrochemically obtaining oxygen is the electrolysis of water. The theoretical voltage for the electrolytic decomposition of water into H_2 and O_2 is 1.23 V at 25°C, but the high overvoltage at the anode causes an increase of the cell voltage up to a value of 2.2 V in 5 M KOH at j = 100 mA cm^{-2}. This means an energetic efficiency of only 0.135 kg O_2/kwh. Besides, hydrogen formation at the cathode entails a potential risk in areas where portable O_2-generators are used. In order to achieve lower V-levels, better yields, and that only pure oxygen gas be evolved from the cell, various systems have been designed capable of cathodically reducing air oxygen via 4 electrons to give rise to hydroxy ions according to the following reaction:

$$O_2 \text{ (from air)} + 2\ H_2O + 4\ e^- \longrightarrow 4\ OH^- \qquad (3)$$

and simultaneously of anodically oxidizing hydroxy ions to release the same amount of pure oxygen through the opposite reaction:

$$4\ OH^- \longrightarrow O_2 \text{ (pure)} + 2\ H_2O + 4\ e^- \qquad (4)$$

One of these systems is an electrochemical oxygen-separator with a 100 cm^2 Nafion® ion-exchange membrane as the electrolyte [Fujita Y., H. Nakamura and T. Muto, J. Appl. Electrochem., 16 (1986) 935-490].

The cathode was a graphite-powder hot-pressed on Nafion with 10% Pt and 60% PTFE, whilst its other face was coated with Pt to form the anode. By feeding the cathode with an air-flux of 4 l min^{-1}, a j = 100 mA cm^{-2} with a voltage in this cell of 1.25 V at 40°C has been achieved. When the device was operated at 200 mA cm^{-2} it produced 70.9 ml min^{-1} oxygen having a purity of 98.4%. Another more efficient system for the tetraelectronic process has been designed by Tseung A.C.C. and S.M. Jasem [J. Appl. Electrochem., 11, 209 (1981)]. It consists of a H-type cell with carbon-black electrodes spaced apart by a glass-fibre membrane and containing 5 M KOH. In the cathodic compartment, the electrode floats on the KOH solution and is fed with air. These authors achieved voltages of 1.3 V at 25°C and of 1.0 V at 40°C for a j value of 100 mA cm^{-2}, whereby a yield of oxygen of 0.298 kg O_2 kwh^{-1} at 40° was experimentally determined, just the same as the one predicted by theory.

Tseung and Jasem have also described an electrochemical-chemical method intended for the extraction of O_2 from air in 5 M KOH, by using a three-chamber cell [US Patent No. 4,300,987, November 17, 1981]. In the cathodic chamber there

is a graphite-PTFE cathode which floats on the solution and, when fed with air, reduces oxygen to HO_2^- according to equation (1c). By placing a Ni mesh coated with $NiCO_2O_4$ in the intermediate chamber, the electrogenerated HO_2^- chemically decomposes to O_2 according to reaction (2), whereas in the anodic chamber evolution of O_2 occurs (reaction (4) on a $NiCO_2O_4$-PTFE anode. Thus, one achieves that the same amount of oxygen bielectronically reduced in the cathode be recovered in the decomposition chamber plus the anodic chamber. With this system, said inventors have been able to obtain yields of 0.378 and 0.486 kg O_2 kwh^{-1} at 25°C and 40°C, respectively, with voltages (once deducted the ohmic drop) of 1.34 V and 1.40 V at a $j = 100$ mA cm^{-2}.

In all the preceding studies relative to electrochemical separation of oxygen from air in a basic medium, operation has been carried out in the absence of HO_2^- in the neighbourhood of the anode, without taking into account its possible anodic oxidation to generate O_2.

SUMMARY OF THE INVENTION

The present invention comprises a new method capable of separating oxygen from a gas mixture containing it by means of an electrochemical process in which takes part 2 electrons per molecule of purified oxygen. Although the system may be applied to a plurality of oxygen-containing gas mixtures to obtain both pure oxygen or totally or partially deoxygenated gas mixtures, it has been designed thinking in the separation and purification of air oxygen, so that from now on "air" will be referred to as a generic example of any gaseous mixtures to which the present invention may be applied.

According to the present invention, there is provided a bielectronic process, both at a non-gas-diffusion anode and at a gas-diffusion cathode of an electrolytic cell, using an aqueous solution of an electrolyte, for an electrolytic separation of oxygen from an oxygen-containing gas mixture comprising the steps of:

a) bringing an oxygen-containing gas in contact with the gas-diffusion cathode which contains no catalyst for decomposition of hydrogen peroxide, and

b) supplying a potential-difference between the gas-diffusion cathode and the non-gas-diffusion anode, so that

b.1) oxygen is converted into hydrogen peroxide or a conjugated base thereof at the cathode according to a bielectronic process,

b.2) the hydrogen peroxide or the conjugated base thereof is diffused through said electrolyte from the gas diffusion cathode to the anode, and

b.3) the hydrogen peroxide or the conjugated base thereof diffused in b.2 is converted into pure oxygen at the anode according to a bielectronic process.

According to the present invention, there is also provided an apparatus for producing pure oxygen, by means of a bielectronic process, from an oxygen-containing gas mixture, comprising a single compartment undivided electrolytic cell wherein there are arranged an aqueous solution of an electrolyte, at least a gas-diffusion cathode and at least an anode, an inlet to the cathode for

hydrophobic polymer but no decomposition catalyst for hydrogen peroxide, and the anode being a non-gas-diffusion anode stable to components present in the electrolyte.

BRIEF DESCRIPTION OF THE DRAWINGS

A detailed description of preferred embodiments will be given herein below with reference to the following drawings, in which like numbers refer to like elements:

Figure 1 is a schematic diagram of an apparatus according to the present invention; and

Figure 2 is a graph illustrating the values for the yield r (curve a) and the values for the number of electrons n per mole of oxygen evolved (curve b) as a function of elapsed time, according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, both electrodic processes have the feature to be bielectronic, which involves an electrical consumption per kilogram of oxygen lower than in other electrochemical processes.

The operation of this cell is based upon electrogeneration of HO_2^- by cathodic reduction of air-oxygen according to reaction (1c) and its further anodic decomposition generating pure O_2 via 2 electrons:

$$HO_2^- + OH^- \longrightarrow O_2 \text{ (pure)} + H_2O + 2\ e^- \qquad (5)$$

The same amount of oxygen reduced at the cathode is released at the anode, i.e, the separation/purification

O_2 (air) ——→ O_2 proceeds through a bielectronic overall process.

The absence of a catalyst for decomposition of hydrogen peroxide at the gas-diffusion cathode prevents the tetraelectronic reaction from O_2 to H_2O.

The pH of the electrolyte is normally high. Nevertheless, we have realized that the generation of hydrogen peroxide may be performed with a good yield from pH 2.5 upwards, whereby the scope of this invention includes any electrolytes having a pH equal to or higher than 2.5, although a pH higher than 11 is preferred in order to avoid corrosion problems and to allow using an alkali as a background-electrolyte (Li-, Na-, K- ... hydroxides) due to its high conductivity at moderate concentrations. Suitable concentrations range from 0.1 M to 10 M, although values between 0.5 and 6 M are preferred. Under such circumstances, the cathodic (1c) and anodic (5) reactions are exactly opposite, as seen before.

Whilst in the process no negative incidence by the air employed has been observed, it is obvious that it will be advantageous to filtrate and purify said inlet-gas in the usual manner like in other obtention processes starting from atmospheric oxygen. Particularly, carbon dioxide and certain acidic pollutants present in the air entail a danger to an alkaline electrolyte because they may, for instance, degrade it by carbonation.

Fortunately, a solution of the alkali itself may efficiently act as a gas washer by previously removing such undesired components. In practice, this means a new usefulness for the used electrolyte which may be in this way reused until its pH is lowered down to 10, its further

treatment as waste water being easier and less expensive. Anyhow, provided that suitable precautions are taken there is no reason to suppose that the same electrolyte could not be used indefinitely. Consequently, the process is a safe and environmentally acceptable one.

The air pressure on the cathode in not significantly higher than one atmosphere. Nevertheless, a higher partial pressure of the inlet-oxygen is of benefit to the process which may be performed with inlet-gas pressures ranging from the atmospheric pressure to 100 bar, preferably from 1 to 10 bar. For the same reason, it is beneficial to suck the outlet-oxygen. Oxygen produced at the anode may be recovered or sucked at a pressure ranging from the atmospheric one to 0.01 bar, preferably from 1 to 0.1 bar. The only significant impurity in said oxygen is moisture, which may be removed by means of conventional condensation or drying equipments.

Since hydrogen peroxide is generated in the cathode, transported towards the anode an oxidized therein, it will be obvious to anyone skilled in the art that in the solution a steady concentration is finally reached which will not vary unless some parameters such as current-density, electrolyte concentration or temperature are modified. However, achievement of this stationary state may be very slow and hence it will be advantageous to initially add such an amount of H_2O_2 that its concentration remains constant during the process. In this way, the steady state may be reached immediately.

Commercial H_2O_2 solutions are known to contain, normally, small concentrations of stabilizers such as urea, diphosphates, tin compounds, acetanilide, alcohol, etc. Generally they are sequestering agents able to catch the small amounts of transition metals, e.g. iron, that catalyze

decomposition of hydrogen peroxide. It has been ascertained that addition of some of these compounds allows to increase the yield of the process.

It has been proved that the process operates better at temperatures above room temperature, such as it is the case in many other electrolytic processes. The device may operate between 0 and 100 °C. In those systems running under pressure it is possible to operate at temperatures above 100°C. Nevertheless, when oxygen evolves through the electrolyte, and in order to obtain it in a not excessively wet condition, it is preferable to use moderate temperatures, between 20 and 50 °C.

The designed system consists of a single-compartment cell containing a cathode of carbon which is agglomerated by means of a hydrophobic polymer, e.g. PTFE, polyethylene or polyvinyl chloride (PVC), with no other catalyst (addition of Pt or a metal-oxide such as perowskyte produces the tetraelectronic reaction of O_2 to H_2O that is intended to be avoided), feeding with air, an anode stable under the process conditions, and an alkali solution.

Fig. 1 relates to the invention's equipment which will be next described. It comprises a Ni-CT thermostatted cell used for the electrolytic separation of oxygen from air. Said equipment is only one among all possible within the scope of this invention and it has been chosen because it is the one used in the experiments provided as examples.

The electrolytic cell consisted of a cylindrical glass tube 1 with an external thermostatization jacket 2, with an inlet 3 and an outlet 4 of water directed to the thermostat, and an upper outlet tube 5 for collecting oxygen gas and for sampling. Through each tube-end, electrodic

supports 6 and 7 are introduced which are fitted with bakelite threads. Each support was a polypropylene hollow-cylinder and in its internal end was placed the corresponding electrode, cathode 8 and anode 9, which were connected to a conventional continuous-power supply through conduction wires 10 and 11.

The anode may be of any conducting material, stable and capable of oxidizing hydrogen peroxide to oxygen, e.g., metals, alloys, conducting metal-oxides, graphite or carbon-PTFE. In the design shown in Fig, 1, the anode was a Ni sheet, but carbon-PTFE anodes have also been used with good results. Anodes containing a catalyst for decomposition of H_2O_2 such as Pt, perowskytes or certain compounds of transition metals such as e.g. Fe (III) or Ni (II), have been also used.

The CT cathode was a mixture of carbon-PTFE, with no other catalyst, hot-pressed on a Ni mesh. The active carbon-PTFE surface is in contact with the solution, whereas the Ni mesh acts as a distributor of the electric current and is in contact with the Ni-Cr connection wire. For preparing the carbon-PTFE, 75% carbon black and a 25% PFTE dispersion were mixed. The resulting mixture was dried at 240°C and crushed with a mill. Following hot-pressing the cathodes used herein had a thickness of about 0.4 mm. While electrodes of up to 5 mm in thickness may be used, thicknesses of 0.1 mm and 0.5 mm are preferred for an easier diffusion of oxygen therethrough.

The Ni anode and the CT cathode were fitted to their corresponding supports by means of polypropylene threads with a cylindrical central opening. The surface area of each electrode in contact with the KOH solution was of 0.785 cm^2.

The air necessary to feed the carbon-PTFE cathode (CT) was supplied by a low-power compressor which produced a 140 ml min^{-1} flux through a glass tube 12 within the cathodic support, the remaining gas being discharged to the atmosphere. Consequently, in this configuration the air pressure on the cathode was not significantly greater than one atmosphere.

The cell used herein included no device for stirring the electrolyte, since this is not necessary for its performance. Nevertheless, evidence has been found of control by diffusion in the anodic oxidation of hydrogen peroxide at low concentrations, for which reason any device for stirring or recycling the electrolyte should be of benefit for the process.

In another design containing a recycling device, a porous anode (e.g. grid, mesh or metallic gauze, or a sintered material) should be used through which the passage of electrolyte would be forced in opposite direction to the cathode. This flux would have the further advantage of drawing out the oxygen bubbles formed and allowing a closer approach between electrodes.

Nevertheless, a porous anode may also be advantageously used without recycling if it is placed horizontally over, and close to, the cathode. In this case, the gravity itself provides for drawing the gas bubbles out of the interelectrodic area where interferences, short-circuits, conductivity decreases and/or undesired side reactions could occur. Such harmful effects were observed in the cell of Fig. 1 when the distance between electrodes was lower than 5 mm and for this reason such distance has been the one used in most experiments. However, this distance, which may range from 0.1 to 10 mm, should be conveniently reduced whenever

the design allows it, operating between 0.1 and 1 mm being preferred. The nearness between electrodes allows to operate whit lower alkali concentrations which, in turn, are compatible with higher HO_2^- concentrations that improve the yield of the process and reduce the voltage of the cell.

Another useful accessory for the present device is a thin permeable membrane or diaphragm between the electrodes (e.g. of paper, cloth, asbestos, glass or a plastic lattice) whose function is to separate them in order to prevent short-circuits while maintaining them close to each other for minimizing transport difficulties of the species in solution as well as losses by ohmic drop. A suitable design for this device should permit using it as a turbulence-promoter with the same purpose.

In a cell like the one used, HO_2^- is electrogenerated from the reduction of air O_2 according to reaction (1c). When operating at sufficiently low voltages, preferably from 0.1 to 1 V, reduction of H_2O (energetically less favourable) does not occur; at the cathode only HO_2^- is generated and the overall process in the cell will be bielectronic. However, oxidation of OH^- ion according to reaction (4) and of HO_2^- ion according to reaction (5) may simultaneously occur at the anode. In the absence of HO_2^- only the OH^- discharge will occur and n will be 4, whereas when HO_2^- electrodecomposes n will vary from 2 to 4. The object of the device presented is to reach a steady state operation which produces oxygen at potentials lower than 1 V and with a consumption of 2 electrons per molecule of purified oxygen. From voltage values of 0.2 V upwards some current-density has been observed and hence oxygen starts to be generated.

The exhaust gas arising from cathode is an oxygen-impoverished or oxygen-devoid air which may be applied, for

instance, in inerting processes. The mixture of part of this gas with pure oxygen arising from anode allows to obtain oxygen-enriched mixtures at any concentration between 21 and 100%. These mixtures find, among others, possible uses in hospitals and may promote combustions and oxidations which otherwise should be difficult in ordinary air. They are also employed in the smelting of certain metals.

The present invention provides improvements over prior works. The experimental tests performed have allowed to improve the results obtained with previous devices. Particularly, voltages to be applied for obtaining a determined pure oxygen flux have been reduced, and the energetic efficiency of the process has been markedly increased, as shown in the following examples. In order to increase the oxygen fluxes being produced, besides the usual stepping in industrial processes it is also possible to interconnect a sufficient number of individual cells.

The energetic efficiency (r) of oxygen in terms of kg O_2 per kwh consumed may be easily calculated, and it only depends upon the number of electrons consumed per molecule of oxygen evolved (n) and the potential-difference applied. In case of n = 4, i.e. if only the OH^- ion would be oxidized at the anode according to reaction (4) and all the HO_2^- would accumulate in the cell medium, the yield would be:

(6) $$r = 0.298/V$$

where V is the potential in volts. This equation may be applied to conventional oxygen-extraction cells. Contrarily, if all the HO_2^- is oxidized at the anode, as indicated by reaction (5) and n = 2, the yield of oxygen in the cell is:

(7) $$r = 0.596/V.$$

When comparing equations (6) and (7), it is evident that a bielectronic cell possesses twice the energetic yield of oxygen than a conventional tetraelectronic cell for the same value of V, although they operate at a different current-density. On the other hand, the number of electrons, n, may be easily determined by the Faraday's law from the electrical charge consumed and the volume of oxygen evolved from the anode.

EXAMPLES

Example 1

In the cell of Fig. 1, 50 ml of a 2.4 M KOH solution was electrolyzed at a constant current-density of 100 mA cm^{-2} for 10 hours while determining the volume of oxygen gas evolved, the change in HO_2^- and OH^- concentrations, as well as the potential-difference between electrodes. The interelectrodic distance was 5 mm and the temperature 25°C. Fig. 2 represents in the Y-axis on the right of the figure the values for the yield r expressed as kg O_2 kwh^{-1} (curve b) and in the Y-axis on the left of the figure the values for the number of electrons n per mole of oxygen evolved (curve a), and in abscissae the time elapsed expressed in hours. In this Figure, it may be observed that the number of electrons per mole of oxygen evolved from the cell gradually decreases from n = 4 (initial time) to n = 2.17 after 10 hours electrolysis. This result indicates an increase of the electrodeposition rate of HO_2^- as its concentration in the medium grows. Moreover, it may also be observed that voltage also decreases from an initial value of 1.21 V to a final value of 1.10 V. This fact, together with the decrease of n, causes a gradual increase of r from 0.247 to 0.495 kg O_2 kwh^{-1} during the electrolysis time. The final HO_2^- concentration was 0.15 M, in agreement with the observed

decrease for OH^- concentration.

Example 2

In the same cell as in Example 1, 50 ml of a solution of 2,4 M KOH and 0,18 M HO_2^- was electrolyzed at constant current-densities of 38, 100 and 191 mA cm^{-2} for 9 hours, the volume of oxygen gas evolved, the change in HO_2^- and OH^- concentrations, as well as the variation in voltage, being all determined. The interelectrodic distance was 5 mm and the temperature 25°C. At 38 mA cm^{-2} voltage remained unchanged between 0.68 V and 0.72 V, at 100 mA cm^{-2} between 1.02 V and 1.05 V, whereas at 192 mA cm^{-2} it gradually diminished from 1.61 V to 1.46 V after 9 hours electrolysis. The volume of oxygen evolved was in very good agreement with the one predicted by theory assuming n = 2 for j = 38 and 100 mA cm^{-2}, conditions under which the composition of the medium scarcely varied during electrolysis. However, the agreement is not good for j = 191 mA cm^{-2}. In this case, the value of n gradually decreased along with electrolysis time from 2.38 to 2.05, whereas 4.5 millimole of HO_2^- were built-up in the medium, which proves that at this current-density the steady state corresponds to a peroxide concentration higher than 0.2 M.

Example 3

Similar experiments to those of Example 2 were carried out with different electrolyte compositions and at different temperatures, by applying constant current-densities of 38 and 100 mA cm^{-2} for periods from 1 to 3 hours. In Table 1 , cell-voltages, mean values of n as determined from the volume of oxygen obtained every 10 minutes of electrolysis, and energetic efficiencies of oxygen obtained for n = 2 (as experimentally determined) are

summarized.

Table 1. Values for n, and yield of oxygen (r) as determined for different Ni-CT cells operating at an almost-steady state, at a constant current-density

[KOH]/M	$[HO_2^-]$/M	Temp./°C	j/mA cm^{-2}	Voltage/V	n	r
0.8	0.121	25	38	0.89	1.99	0.671
	0.216	25	38	0.57	2.01	1.047
	0.381	25	38	0.52	1.96	1.148
		25	100	1.02	2.05	0.585
		35	100	0.90	2.00	0.663
		45	100	0.86	1.95	0.694
2.4	0.124	25	38	0.76	1.97	0.786
	0.185	25	38	0.68	1.99	0.878
		25	100	1.02	2.00	0.585
		35	100	0.90	1.97	0.663
		45	100	0.82	1.97	0.728
	0.266	25	100	0.98	2.03	0.609
		35	100	0.85	1.96	0.702
		45	100	0.77	1.98	0.775
	0.459[a]	25	100	0.73	1.98	0.816

[a] The electrolyte contained urea at a concentration of 1.5 mM.

As it may be seen in Table 1, at constant current-density and temperature the yield of oxygen noticeably increases with HO_2^- concentration. Upon increasing temperature, a decrease of cell voltage occurs, and the yield of oxygen also increases.

The Ni-CT cell may operate at current-densities of 100 mA cm^{-2} by applying voltages of 0.98 V at 25°C to give an oxygen yield of 0.609 kg O_2 kwh^{-1}. This value is significantly higher than the yields of 0.378 an 0.486 kg O_2 kwh^{-1} at 100 mA cm^{-2} obtained by Tseung and Jasem at 25°C and 40°C, respectively, which are the best values found in the literature for the electrolytic obtention of oxygen. Our best yield at 100 mM cm^{-2} has been 0.815 kg O_2 kwh^{-1} at 45°C. In this test a small amount of urea was added to the solution. At lower current-densities, yields higher than 1 kg O_2/kwh may easily be obtained, even at room temperature.

Example 4

In this case, the same cell as in the preceding Examples was used, but fitted with a CT instead of a Ni anode. For comparative purposes, a CT-CT cell under the same conditions than the Ni-CT cell, at 25°C and 5 mm inter-electrodic distance, has been studied. The almost stationary j-V curve of a CT-CT cell with 0.8 M KOH and 0.46 M HO_2^- has been found to have a smaller slope than that of an analogous Ni-CT cell, so that the former is better than the later at voltages under 0.6 V. Thus, while in a CT-CT cell a voltage of 0.48 V for j = 38 mA cm^{-2} is only needed, in the CT-CT cell 0.55 V is required to obtain the same current-density with a Ni anode. Nevertheless, it is necessary to apply 1.55 V for a current of 100 mA cm^{-2} to circulate through the CT-CT cell, i.e. about 0.50 V more than for a Ni-CT cell.

Moreover, volumes of oxygen evolved from the solution are small: 3 ml at 38 mA cm^{-2} and 7.5 ml at 100 mA cm^{-2}, where the respective volumes for n = 2 should be 13.7 ml and 36.6 ml, respectively. This fact indicates that

most of the oxygen generated in the CT anode diffuses through it instead of being evolved through the solution, which would permit its extraction by means of an aspirator, with a minimum degree of moisture.

WHAT IS CLAIMED IS:

1. A bielectronic process, both at a non-gas-diffusion anode and at a gas-diffusion cathode of an electrolytic cell, using an aqueous solution of an electrolyte, for an electrolytic separation of oxygen from an oxygen-containing gas mixture comprising the steps of:

a) bringing an oxygen-containing gas in contact with the gas-diffusion cathode which contains no catalyst for decomposition of hydrogen peroxide, and

b) supplying a potential-difference between the gas-diffusion cathode and the non-gas-diffusion anode, so that

b.1) oxygen is converted into hydrogen peroxide or a conjugated base thereof at the cathode according to a bielectronic process,

b.2) the hydrogen peroxide or the conjugated base thereof is diffused through said electrolyte from the gas diffusion cathode to the anode, and

b.3) the hydrogen peroxide or the conjugated base thereof diffused in b.2 is converted into pure oxygen at the anode according to a bielectronic process.

2. The process according to claim 1, wherein the potential-difference between the anode and the cathode is sufficiently low as not to cause

reduction of water, and ranges from 0.1 V to 1 V.

3. The process according to claim 1 or 2, wherein the process is performed at temperatures ranging from 20 to 50°C.

4. The process according to claim 1, wherein a pressure of the oxygen-containing gas mixture ranges from 1 bar to 100 bar.

5. The process according to claim 4, wherein the pressure of the oxygen-containing gas mixture ranges from 1 to 10 bar.

6. The process according to claim 1, wherein said pure oxygen produced in b.3 is collected or sucked at a pressure ranging from ambient pressure to 0.01 bar.

7. The process according to claim 6, wherein the pressure ranges from 1 to 0.1 bar.

8. The process according to claim 1, wherein said pure oxygen produced in b.3 is collected or sucked through said anode.

9. The process according to claim 1, wherein the electrolyte contains a Li-, Na- or K- hydroxide.

10. The process according to claim 9, wherein the electrolyte has a concentration of the Li-, Na- or K- hydroxide ranging from 0.1 M to 10 M.

11. The process according to claim 10, wherein the concentration of the Li-, Na- or K- hydroxide ranges from 0.5 M to 6 M.

12. The process according to claim 9 or 11, wherein an initial amount of hydrogen peroxide is added to the electrolyte so that a concentration thereof remains stable during the process.

13. The process according to claim 9, 10, 11 or 12, wherein an amount lower than 10 mM of a metal-sequestering agent is added to the electrolyte.

14. The process according to claim 13, wherein the metal-sequestering agent is urea.

15. An apparatus for producing pure oxygen, by means of a bielectronic process, from an oxygen-containing gas mixture, comprising a single compartment undivided electrolytic cell wherein there are arranged an aqueous solution of an electrolyte, at least one gas-diffusion cathode and at least one anode, an inlet to the cathode for the oxygen-containing gas mixture and an outlet for oxygen produced in the cell, said cathode containing a hydrophobic polymer but no decomposition catalyst for hydrogen peroxide, and the anode being a non-gas-diffusion anode stable to components present in the electrolyte.

16. The apparatus according to claim 15, wherein the electrolytic cell comprises an external

thermostatization jacket adequate to maintain a constant temperature.

17. The apparatus according to claim 15, further comprising a device for stirring or recycling said electrolyte.

18. The apparatus according to claim 15, wherein said cathode is up to 5 mm in thickness.

19. The apparatus according to claim 18, wherein said cathode is from 0.1 to 0.5 mm in thickness.

20. The apparatus according to claim 15, wherein a distance between the cathode and the anode ranges from 0.1 to 10 mm.

21. The apparatus according to claim 20, wherein the distance between the cathode and the anode ranges from 0.1 to 1 mm.

22. The apparatus according to claim 15, wherein the non-gas-diffusion anode is made of conducting material, stable under conditions of the bielectronic process and capable of oxidizing oxygen peroxide to oxygen, said material including metals, alloys, conducting metal-oxides, graphite or carbon-polytetra-fluoroethylene.

23. The apparatus according to claim 22, wherein the anode made of said material is a porous anode.

24. The apparatus according to claim 23, wherein the porous anode is a grid, mesh, or metallic gauze, or a sintered conducting material.

25. The apparatus according to claim 20, wherein the anode is a porous anode, and the porous anode is a grid, mesh, or metallic gauze, or a sintered conducting material.

26. The apparatus according to claim 23 or 25, wherein the porous anode is horizontally arranged over, and in proximity to, the cathode.

27. The apparatus according to claim 15, wherein the anode and the cathode are arranged so that said electrolyte flows through the anode in an opposite direction to the cathode and draws along therewith the oxygen being produced.

28. The apparatus according to claim 15, further comprising a thin permeable membrane or diaphragm, made of paper, cloth, asbestos, glass or of a plastic lattice, between the anode and the cathode.

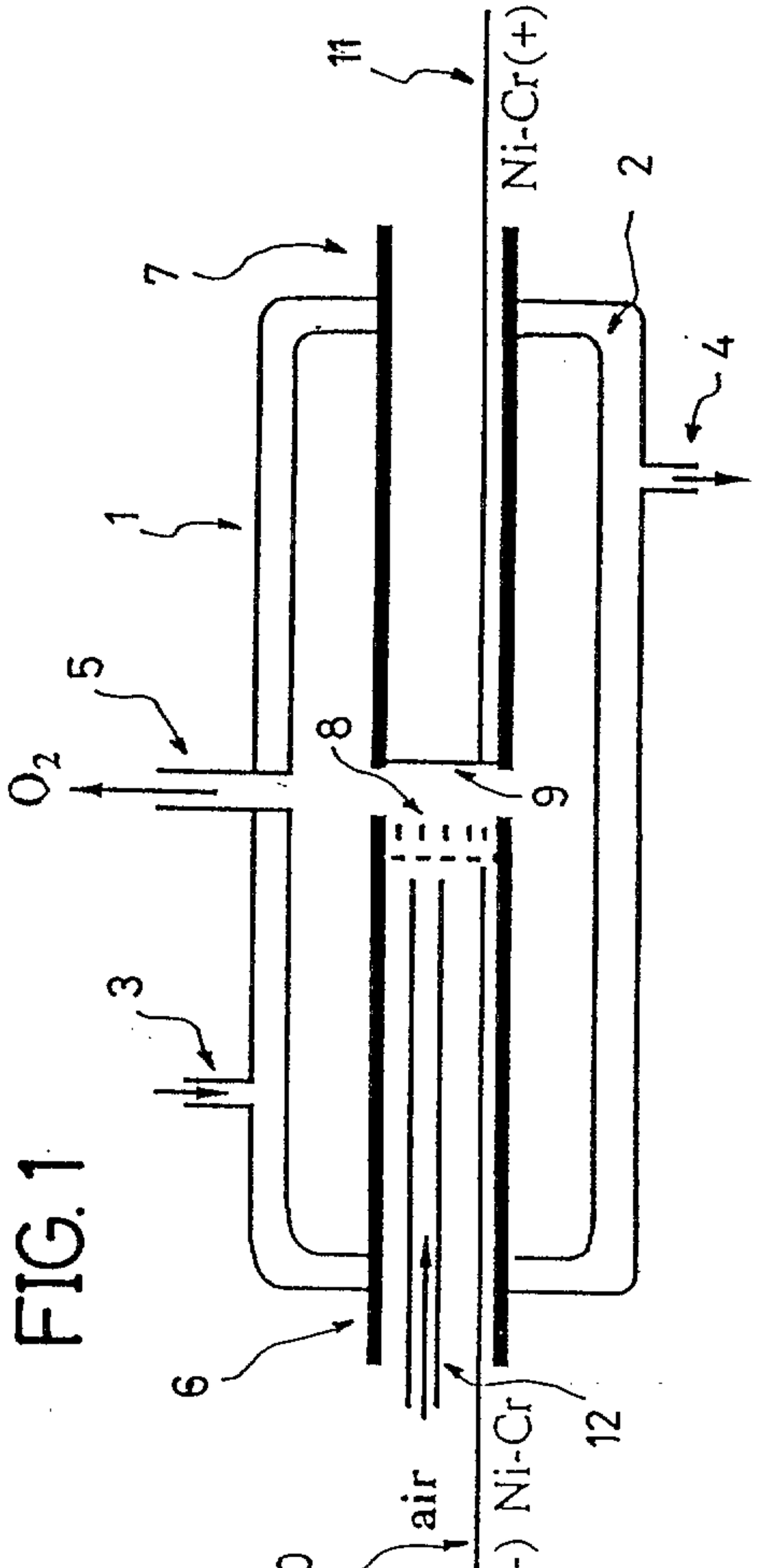
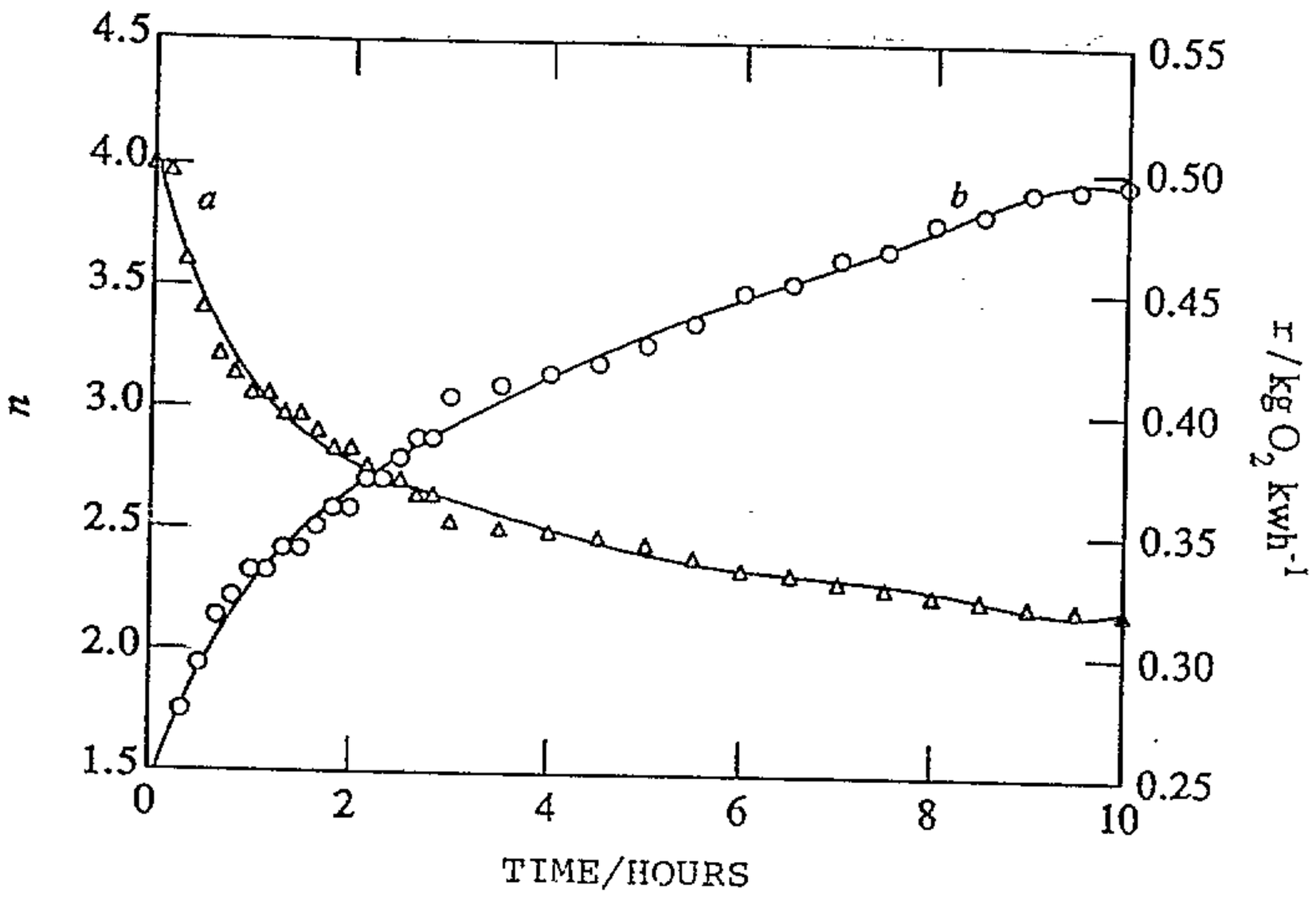


FIG. 1

FIG. 2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3.0
2.5
2.0
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n
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b
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0.30
0.25
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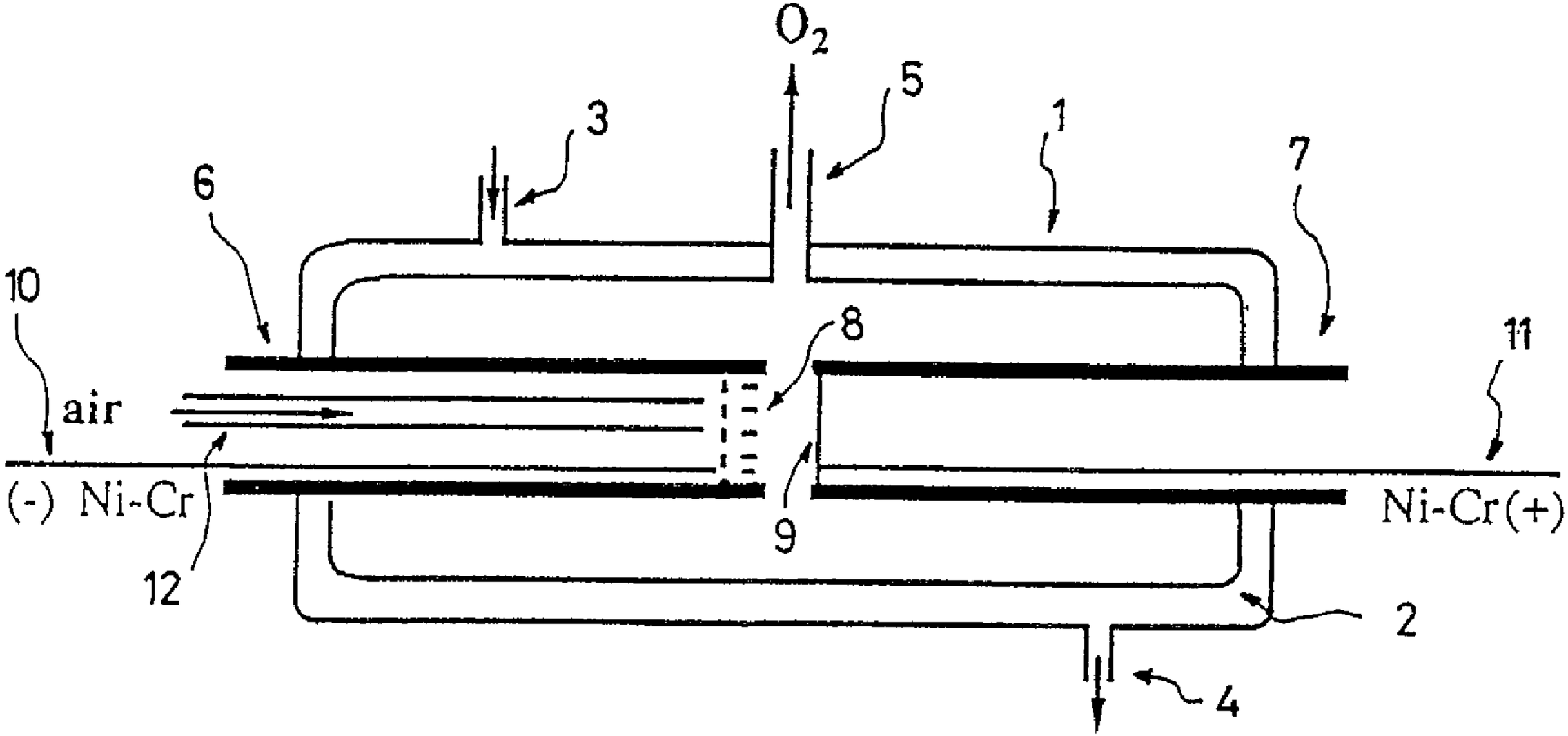
4
6
8
10
TIME/HOURS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7
6
10
8
11
air
(-) Ni-Cr
Ni-Cr(+)
9
12
2
4