

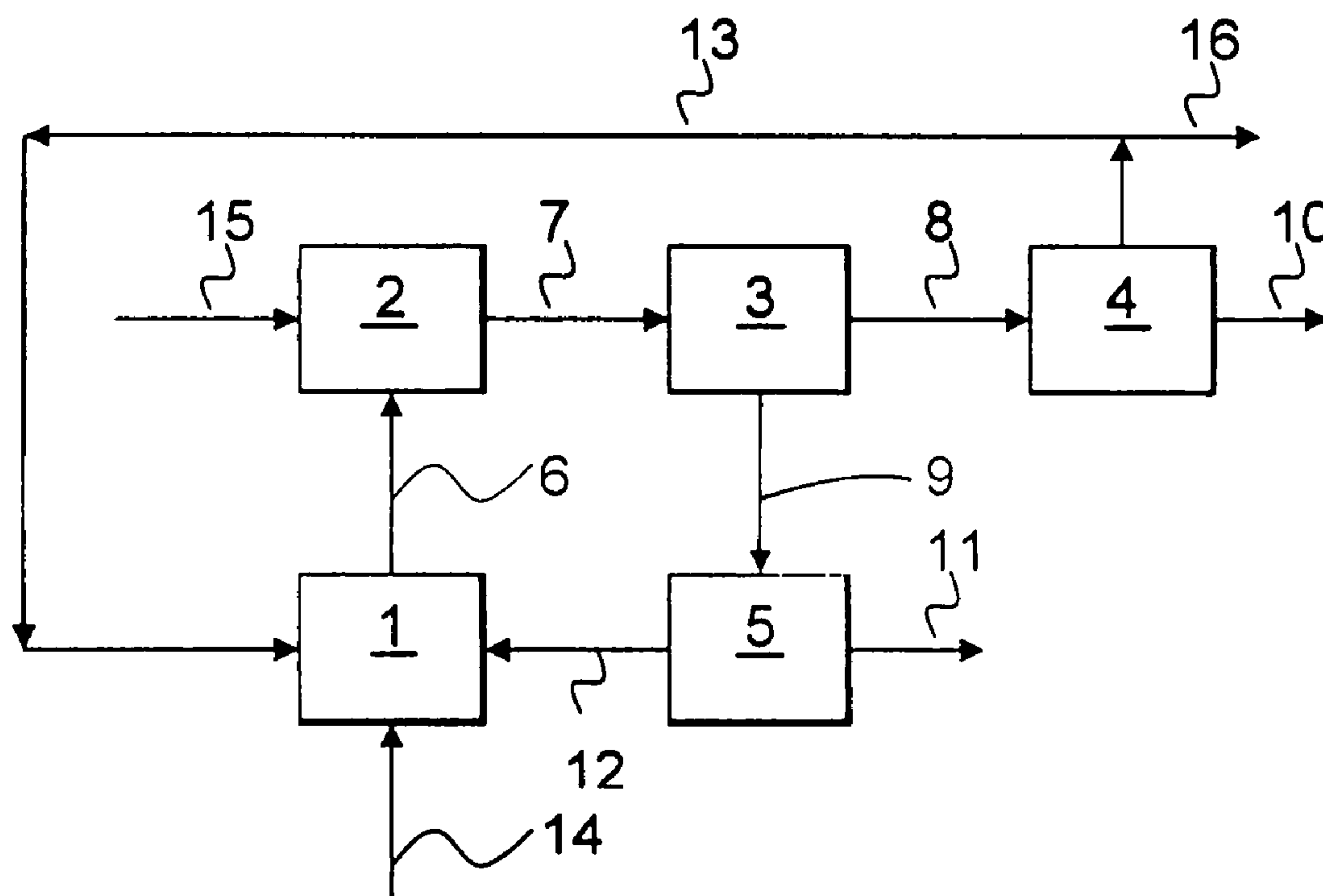
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**Edvinsson Albers et al.**(10) **Pub. No.: US 2007/0012578 A1**(43) **Pub. Date: Jan. 18, 2007**(54) **CHEMICAL PROCESS****Publication Classification**(75) Inventors: **Rolf Edvinsson Albers**, Partille (SE);  
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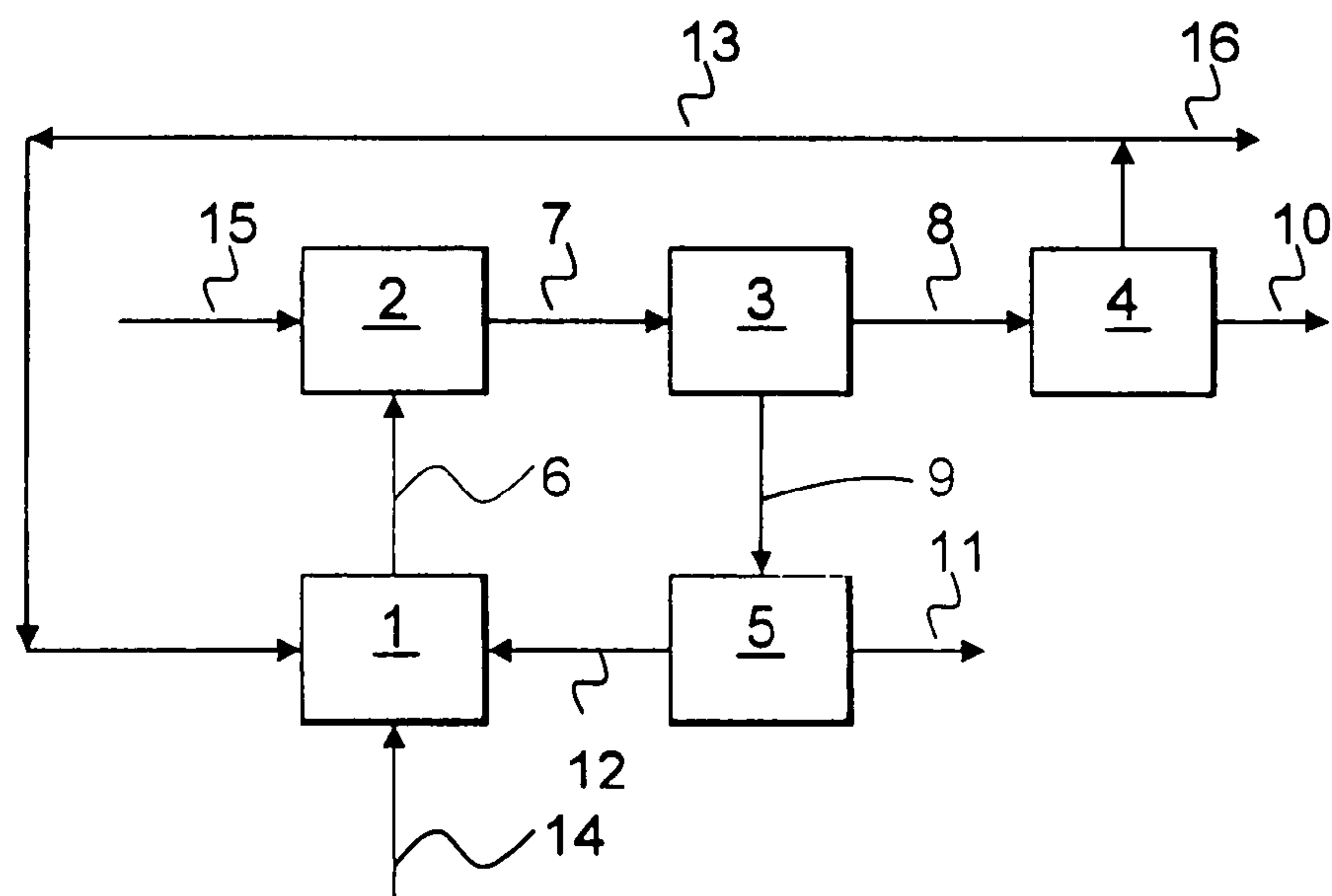
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**ALEXANDRIA, VA 22314 (US)**(73) Assignee: **Akzo Nobel N.V.**, SB Arnhem (NL)(21) Appl. No.: **11/477,150**(22) Filed: **Jun. 29, 2006****Related U.S. Application Data**(60) Provisional application No. 60/694,982, filed on Jun.  
30, 2005.(57) **ABSTRACT**

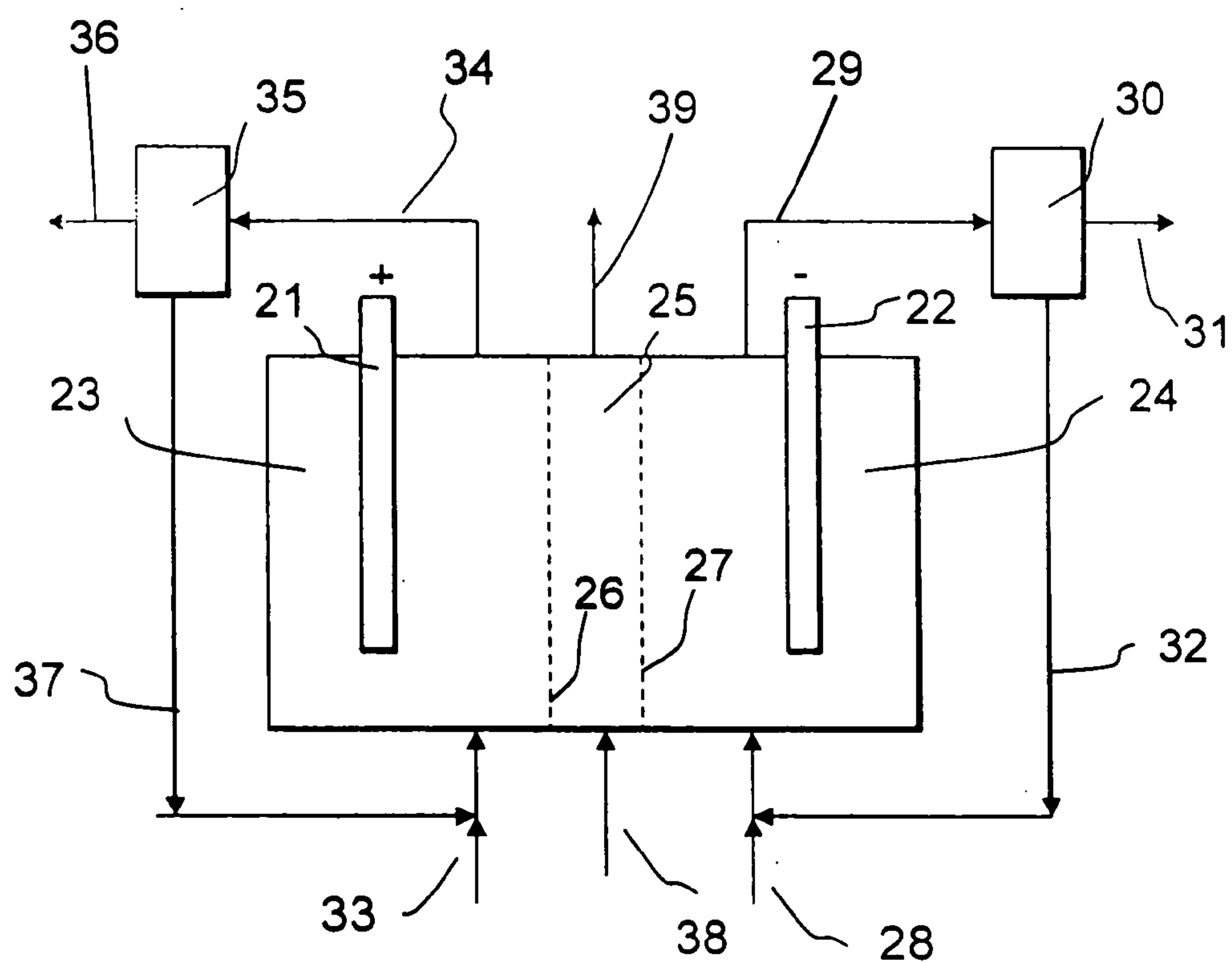
The invention relates to a process for the production of hydrogen peroxide comprising: providing an electrochemical cell comprising an anode and a cathode; contacting the cathode with an electrolyte comprising at least one organic mediator dissolved in an at least partially organic continuous liquid phase comprising an at least partially organic salt and a neutral co-solvent, said salt comprising at least one kind of organic cation and/or organic anion, said continuous liquid phase having an electrical conductivity under process conditions of at least about 0.1 S/m; reacting the organic mediator at the cathode to form at least one reduced form of the mediator; and, reacting the at least one reduced form of the mediator with oxygen to form hydrogen peroxide.



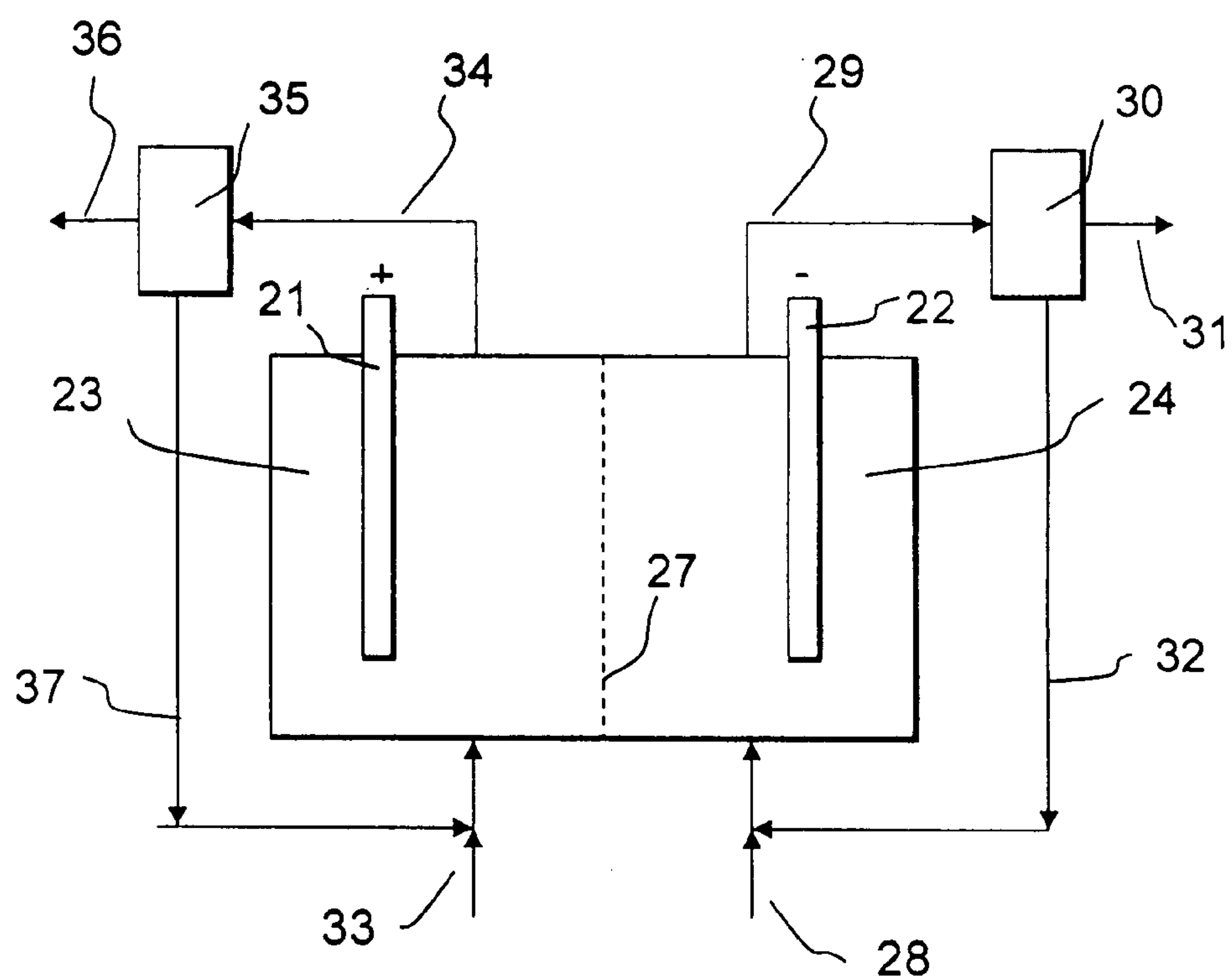
**Fig. 1**



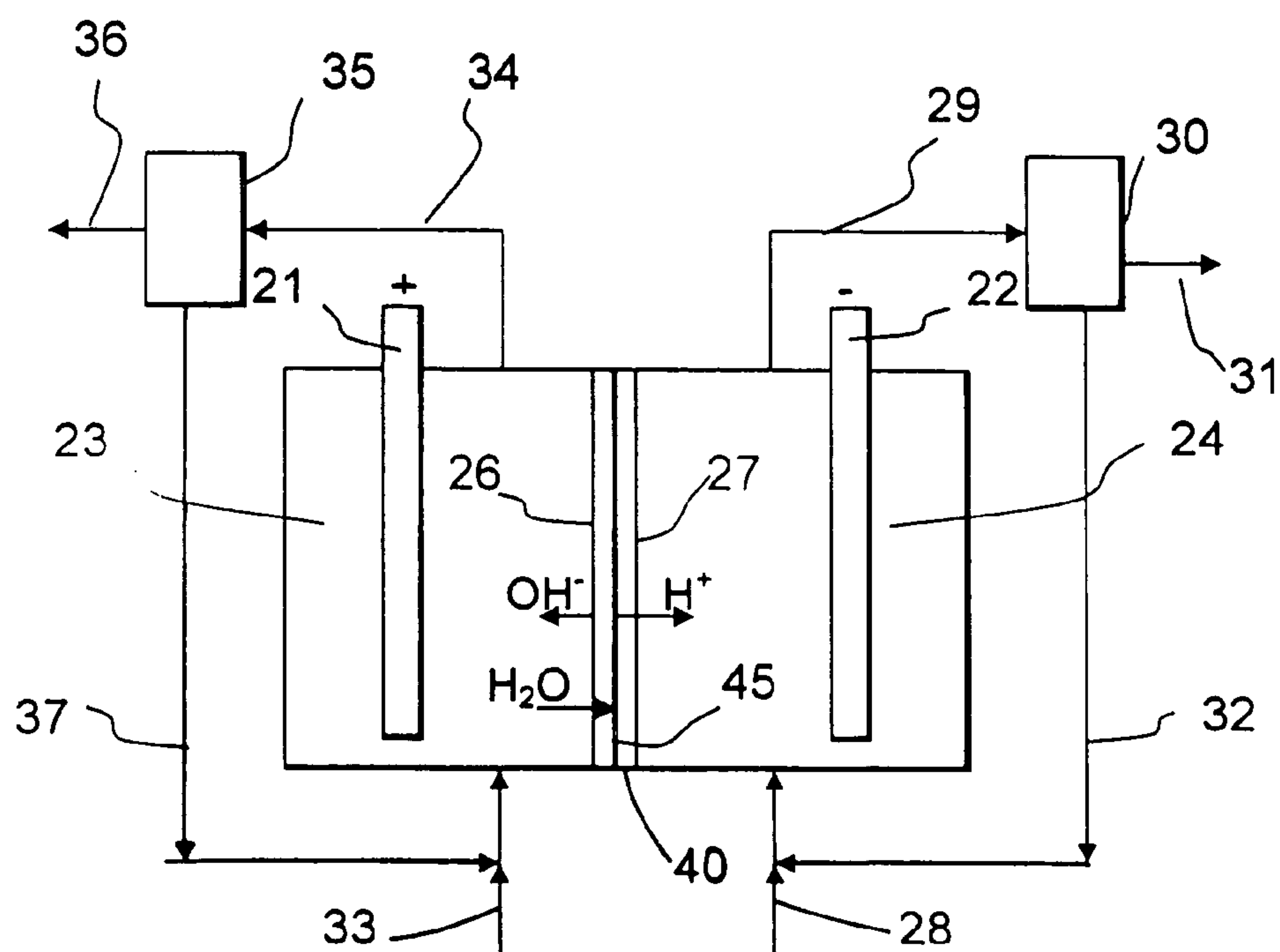
**Fig. 2**



**Fig. 3**



**Fig. 4**





**CHEMICAL PROCESS**

[0001] The present invention relates to a process for the production of hydrogen peroxide by reacting an organic mediator at a cathode to form a reduced mediator and reacting the reduced mediator with oxygen to form hydrogen peroxide.

[0002] The most common process for commercial production of hydrogen peroxide is the anthraquinone process involving alternate hydrogenation and oxidation of anthraquinones and/or tetrahydro anthraquinones in a working solution. Although very efficient, this process is complicated to operate and requires extensive equipment. Alternative processes have so far not been proved competitive for large scale production of hydrogen peroxide.

[0003] Electrochemical production of alkaline hydrogen peroxide solution by reducing oxygen on a cathode is disclosed in e.g. U.S. Pat. No. 6,322,690.

[0004] Electrochemical production of alkaline hydrogen peroxide solution by reducing oxygen on a cathode and simultaneous production of sodium chlorate is disclosed in E. E. Kalu and C. Oloman, "Simultaneous electrosynthesis of alkaline hydrogen peroxide and sodium chlorate", *Journal of Applied Electrochemistry* 20 (1990), 932-940.

[0005] E. L. Gyenge and C. W. Oloman disclose in "Electrosynthesis of hydrogen peroxide in acidic solutions by mediated oxygen reduction in a three-phase (aqueous/organic/gaseous) system Part I: Emulsion structure, electrode kinetics and batch electrolysis", *Journal of Applied Electrochemistry* (2003), 33(8), 655-663 and "Electrosynthesis of hydrogen peroxide in acidic solutions by mediated oxygen reduction in a three-phase (aqueous/organic/gaseous) system. Part II: Experiments in flow-by fixed-bed electrochemical cells with three-phase flow", *Journal of Applied Electrochemistry* (2003), 33(8), 665-674, production of hydrogen peroxide by electroreduction of 2-ethyl-9,10-anthraquinone to the corresponding anthrahydroquinone dissolved in an organic phase emulsified in water. The anthrahydroquinone is reacted with gaseous oxygen to obtain hydrogen peroxide.

[0006] JP 61-284591 and U.S. Pat. No. 4,067,787 disclose production of hydrogen peroxide by reduction of a water soluble anthraquinone derivate in an aqueous solution followed by reaction with oxygen.

[0007] A. Huissoud and P. Tissot disclose in "Electrochemical reduction of 2-ethyl-9,10-anthraquinone on reticulated vitreous carbon and mediated formation of hydrogen peroxide" *Journal of Applied Electrochemistry* (1998), 28(6), 653-657, electrochemical reduction of 2-ethyl-9,10-anthraquinone in dimethoxyethane comprising 5% water and 0.1 mole/litre of tetraethyl ammonium tetrafluoroborate.

[0008] Electrochemical reduction of oxygen on a carbon cathode grafted with anthraquinone is disclosed in e.g. WO 02/02846, Mirkhalaf, Fakhradin; Tammeveski, Kaido; Schiffrin, David J., "Substituent effects on the electrocatalytic reduction of oxygen on quinone-modified glassy carbon electrodes", *Phys. Chem. Chem. Phys.* (2004), 6(6), 1321-1327, and Vaik, Katri; Schiffrin, David J.; Tammeveski, Kaido; "Electrochemical reduction of oxygen on anodically pre-treated and chemically grafted glassy carbon electrodes in alkaline solutions", *Electrochemistry Communications* (2004), 6(1), 1-5.

[0009] Vaik, Katri; Sarapuu, Ave; Tammeveski, Kaido; Mirkhalaf, Fakhradin; Schiffrin, David J. "Oxygen reduction on phenanthrenequinone-modified glassy carbon electrodes in 0.1 M KOH", *Journal of Electroanalytical Chemistry* (2004), 564(1-2), 159-166, discloses use of a cathode grafted with phenanthrenequinone.

[0010] WO 03/004727 discloses electrosynthesis of organic compounds by electrochemical transformation of a compound in the presence of an electrolyte comprising a room temperature ionic liquid and recovering the product.

[0011] It is an object of the invention to provide a process for the production of hydrogen peroxide that can be performed in comparatively simple equipment.

[0012] It is another object of the invention to provide a process for the production of hydrogen peroxide involving electrochemical reduction of a mediator.

[0013] It is still another object of the invention to provide a process for the production of hydrogen peroxide by indirect electrochemical oxygen reduction without the need for contacting a cathode with gaseous oxygen.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0014] For a fuller understanding of the invention, the following description should be read in conjunction with the drawings, wherein:

[0015] FIG. 1 is a schematic of a cathodic process;

[0016] FIG. 2 is a schematic of one embodiment of an electrolytic cell of the invention;

[0017] FIG. 3 is a schematic of another embodiment of an electrolytic cell of the invention; and

[0018] FIG. 4 is a schematic of yet another embodiment of an electrolytic cell of the invention.

[0019] According to the invention it has been found possible to fulfil these objects in a process for the production of hydrogen peroxide comprising:

providing an electrochemical cell comprising an anode and a cathode;

[0020] contacting the cathode with an electrolyte comprising at least one organic mediator dissolved in an at least partially organic continuous liquid phase having an electrical conductivity under process conditions of at least about 0.1 S/m, more preferably at least about 1 S/m, most preferably at least about 3 S/m;

reacting the organic mediator at the cathode to form at least one reduced form of the mediator; and,

reacting the at least one reduced form of the mediator with oxygen to form hydrogen peroxide.

[0021] The organic mediator is a substance capable of being electrochemically reacted at a cathode to yield one or several reduced forms, which in turn are capable of reacting with preferably molecular oxygen and be converted back to the original form, thus enabling a cyclic process. The reaction of the reduced forms of the mediator with oxygen preferably take place in the presence of protons. However, in the absence of a suitable proton source it is possible to form peroxide salts, for example  $\text{Na}_2\text{O}_2$ , which subsequently may be hydrolyzed to yield hydrogen peroxide. Without being



bound to any theory it is believed that the reaction scheme yielding hydrogen peroxide comprises the transfer of two electrons and two protons taking place in separate or combined simultaneous reactions and is believed to involve as intermediate species  $O_2^-$ ,  $HOO^-$ , and  $HOO^-$ .

[0022] Examples of classes of organic substances forming redox systems and useful as mediators include quinones, flavoquinones, pyridine derivatives such as nicotineamides, and ketones.

[0023] Useful quinones include molecules containing a (benzo)quinone-moiety (ortho- or para-forms), of which anthraquinones, tetrahydro anthraquinones, naphthoquinones, benzoquinones and derivatives thereof are preferred. Anthraquinones, naphthoquinones and benzoquinones are preferably substituted, for example alkyl substituted like 2-alkyl-9,10-anthraquinones. Specific examples include 2-ethyl-9,10-anthraquinone, 2-tert-butyl-9,10-anthraquinone, 2-hexenyl-9,10-anthraquinone, eutectic mixtures of alkyl-9,10-anthraquinones, mixtures of 2-amyl-9,10-anthraquinones, all of which having high stability. Specific examples of alkyl substituted naphthoquinones include 2-methyl-1,4-naphthoquinone, 2-ethyl-1,4-naphthoquinone, 2-propyl-1,4-naphthoquinone, 2-tert-butyl-1,4-naphthoquinone, 2-tert-amyl-1,4-naphthoquinone, 2-iso-amyl-1,4-naphthoquinone, 2,3-dimethyl-1,4-naphthoquinone. Other examples of substituents useful for controlling reactivity and solubility of quinones include  $-SO_3H/-SO_3^-$ ,  $-PO_2R^-$ ,  $-OPO_3R^-$ ,  $-NO_2$ ,  $-OCH_3$ ,  $-SO_2CH_3$ ,  $-OPh$ ,  $-SPh$ ,  $-SO_2Ph$ ,  $-COOH/-COO^-$ ,  $-CN$ ,  $-OH$ ,  $-COCH_3$ ,  $-F$ ,  $-Cl$ ,  $-Br$ ,  $-CF_3$ ,  $-NH_2/-NH_3^+$ ,  $-NRH/-NRH_2^+$ ,  $-NR_2/-NR_2H^+$ ,  $-NR_3^+$ ,  $-PH_2/-NH_3^+$ ,  $-SR_2^+$ ,  $-PRH/-PRH_2^+$ ,  $-PR_2/-PR_2H^+$  and  $-PR_3^+$ , R preferably being, independently of each other, optionally substituted alkyl, alkenyl or aryl, or hydrogen. Anthraquinone may be singly or multiply substituted with a combination of the above and/or other substituents. It is also possible to use quinone derivatives having common charge bearing substituents imposing an ionic character of the molecule. Specific examples of non-alkyl substituted quinones derivatives include anthraquinone-2-sulfonate, 5,6,7,8-tetrahydro-9-10-anthraquinone-2-sulfonate, anthraquinone-2,6-disulfonate, naphthoquinone-2-sulfonate, 2-methoxy-1,4-naphthoquinone, 2-ethoxy-1,4-naphthoquinone, 2-amino-anthraquinone, 2-amino-naphthoquinone, 2-(alkyl amino)-anthraquinone, 2-(dialkyl amino)-anthraquinone, 2-(trialkyl ammonium)-anthraquinone, 2-(alkyl amino)-naphthoquinone, 2-(dialkyl amino)-naphthoquinone, 2-(trialkyl ammonium)-naphthoquinone. Naphthoquinones may, e.g. be substituted at any position on the lateral ring, e.g. naphthoquinone-6-sulphonate or 6-trialkylammonium naphthoquinone. One substituent on each ring can also be advantageous, such as 6-amyl-naphthoquinone-2-sulphonate or 6-ethyl-2-triethylammonium naphthoquinone. Corresponding examples for benzoquinone are benzoquinone-2-sulphonate and 2-(ethyl,dimethyl)ammonium. Anthraquinones and naphthoquinones with the lateral rings partially hydrogenated, e.g. 1,2,3,4-tetrahydro anthraquinone, 5,6,7,8-tetrahydro-2-ethyl-anthraquinone, 5,6,7,8-tetrahydronaphthoquinone, could also be used. This also applies to substituted anthra- and naphtho-quinones, including those corresponding to the kinds mentioned above.

[0024] In the case a quinone is substituted and comprise one or more optionally substituted alkyl, alkenyl or aryl groups, it is preferred that these groups independently from each others, have from 1 to 12 carbon atoms, most preferably from 1 to 8 carbon atoms. If of more than one such group is present, they are preferably of mixed chain length. Alkyl, alkenyl and aryl groups may also be substituted, e.g. with one or more hydroxyl group.

[0025] Quinones, including anthraquinones, tetrahydro anthraquinones, naphthoquinones, benzoquinones and derivatives thereof, can be reduced to corresponding hydroquinones by successive addition of two electrons and two protons. Next to the quinone and the hydroquinone a number of intermediate forms are believed to be present and active, like the semi-quinone radical and the semiquinone anion, as well as the base forms of the acidic hydroquinone. All these reduced forms may react with oxygen and contribute to the overall reaction yielding hydrogen peroxide and the original quinone.

[0026] Other mediator systems capable of reducing oxygen to superoxide and subsequently hydrogen peroxide include flavoquinones, e.g. flavin (see e.g. H. Tatsumi et al in "Mechanistic study of the autooxidation of reduced flavin and quinone compounds" in Journal of Electroanalytical Chemistry (1998), 443, 236-242) and pyridine derivatives like nicotinamide and derivatives thereof.

[0027] Further mediator systems are formed by ketones and their corresponding alcohols. The ketone can be electrochemically reduced to the corresponding alcohol, which reacts with oxygen to form hydrogen peroxide and the original ketone. Secondary alcohols are preferred and particularly phenylic ones. Useful alcohols include isopropyl alcohol, benzyl alcohol, diphenylmethanol, methylphenylmethanol. Secondary alcohols also containing a charge bearing group can also be used.

[0028] The content of organic mediator, including the reduced forms, in the at least partially organic continuous liquid phase is preferably at least about 0.1 wt %, more preferably at least about 1 wt %, most preferably at least about 3 wt %. It is limited upwards only by the solubility, which depends on the mediator used and the composition of the liquid phase, but in many cases may be as much as about 10 wt % or about 20 wt % or even higher. In an embodiment where a significant part of the hydrogen peroxide is formed outside the cell the content of organic mediator is preferably at least about 1 wt % to, more preferably at least about 3 wt %, most preferably at least about 10 wt %.

[0029] The at least partially organic continuous liquid phase preferably comprises at least about 20 wt %, more preferably at least about 50 wt %, most preferably at least about 80 wt % of organic components, and may in extreme cases be substantially free from inorganic components. However, it is preferred that at least about 5 wt %, most preferably at least about 20 wt % of inorganic components are included. Such inorganic components may, for example, be inorganic ions from salts made up of both organic and inorganic ions.

[0030] The at least partially organic continuous liquid phase preferably comprises an at least partially organic salt, comprising at least one kind of organic cation and/or organic anion. The content thereof in the continuous liquid phase is



preferably from about 20 wt % to about 99 wt %, more preferably from about 40 wt % to about 95 wt %, most preferably from about 60 wt % to about 90 wt %.

[0031] The at least partially organic salt may be selected from the group of salts referred to as ionic liquids, a diverse class of liquids substantially consisting of ions. An ionic liquid can be simple and contain a single kind of anions and a single kind of cations, or may be complex and consist of a mixture of different anions and/or different cations. Some ionic liquids have a low melting point and negligible vapour pressure near or below room temperature and are often referred to as room temperature ionic liquids. Such ionic liquids usually remain liquids over a large temperature range.

[0032] The at least partially organic salt may also be selected from salts that alone are not classified as ionic liquids but have such properties when present together with a neutral co-solvent such as water or a low molecular alcohol like methanol, ethanol or propanol. The weight ratio salt to co-solvent is preferably from about 1:1 to about 1000:1, more preferably from about 2:1 to about 100:1, most preferably from about 5:1 to about 20:1.

[0033] It is preferred to use an at least partially organic salt that in itself or in combination with a neutral co-solvent forms a liquid phase at atmospheric pressure below about 130° C., preferably below about 100° C., most preferably below about 80° C. Further, the partial pressure of the salt at 100° C. is preferably below about 10 kPa, more preferably below about 1 kPa, most preferably below 0.1 kPa (excluding the partial pressure from an optional neutral co-solvent).

[0034] A liquid with suitable physical properties may comprise one or a mixture of two or more at least partially organic salts, optionally in combination with neutral co-solvents. It may also comprise anions and cations that alone do not form salts with suitable properties.

[0035] The at least partially organic salt may be formed from various combinations of cations and anions, among which at least one kind of ion is organic. The ions are preferably monovalent. Examples of cations include 1-alkyl-3-methyl imidazolium, 1-butyl-3-methyl imidazolium [BMIM], 1-ethyl-3-methyl imidazolium [EMIM], 1,2,3-trimethyl imidazolium, N-alkylpyridinium, N-butyl pyridinium [BPY], pyrrolidinium, guanidinium and alkyl guanidinium, isouronium,  $PR_4^+$ ,  $NR_4^+$ ,  $SR_3^+$ , tetramethylammonium, choline, cocomonium, and mixtures thereof, R preferably being, independently of each other, optionally substituted alkyl, alkenyl or aryl, or hydrogen. Other examples include substituted quinones here denoted  $[Q-NR_3^+]$  and  $[Q-PR_3^+]$ , where Q represents a quinone such as anthraquinone, naphthoquinone or benzoquinones and R being as above. Examples of anions include hexafluorophosphate [HFP], tetrafluoroborate [TFB], fluorosulfonate, hexafluoroantimonate hexafluoroarsenate, chloroaluminate, bromoaluminate, bis(trifluoromethylsulfonyl)imide, tris(trifluoromethylsulfonyl)methide, tricyanomethide, dicyanamide, nonafluorobutanesulfonate, trifluoromethane sulfonate, 2,2,2-trifluoroethanesulfonate, nitrate, sulphate, phosphate,  $RPO_4^{2-}$ ,  $R_2PO_4^-$ ,  $R_2PO_2^-$  (e.g. a dialkylphosphinate), perchlorate, actetate, alkylsulphonate, bis(2-ethyl-hexyl)sodium sulfosuccinate, diethyleneglycolmonomethyl-ethersulfate, alkyloligoethersulfate, pivalate, tetraalkylborate, propionate, succinate, saccharinate, glyco-

late, stearate, lactate, malate, tartrate, citrate, ascorbate, glutamate, benzoate, salicylate, methanesulfonate, toluenesulfonate, and mixtures thereof, R being as above. Other examples include substituted quinones here denoted  $[Q-(O)-SO_3^-]$  and  $[Q-(O)-PO_3R^-]$ , where Q represents a quinone such as anthraquinone, naphthoquinone or benzoquinones, (O) denotes an optional oxygen (e.g. sulphate/sulphonate and phosphate/phosphonate) and R being as above.

[0036] In the case any cation or anion comprise one or more optionally substituted alkyl, alkenyl or aryl groups, it is preferred that these groups independently from each others, have from 1 to 12 carbon atoms, most preferably from 1 to 8 carbon atoms. If of more than one such group is present, they are preferably of mixed chain length. Alkyl, alkenyl and aryl groups may also be substituted, e.g. with one or more hydroxyl group.

[0037] Examples of salts useful for the present invention include any combination of the following cations; [1,3-dialkyl imidazolium], [trialkylammonium], [tetraalkylammonium], [trialkylphosphonium], [tetraalkylphosphonium], [alkylpyridinium], [choline],  $[Q-NR_3^+]$  and  $[Q-PR_3^+]$  in combination with any of the following anions; [sulphate], [phosphate], [alkyl sulphate], [alkyl sulphonate], [dialkyl phosphate], [alkyl phosphonate],  $[Q-(O)-SO_3^-]$  and  $[Q-(O)-PO_3R^-]$ , where Q, (O) and R are defined as above.

[0038] Specific combinations of groups include [1,3-dialkyl imidazolium][alkyl sulphonate] such as any one of [1-butyl-3-methyl imidazolium][methyl- $SO_3^-$ ], [1-ethyl-3-methyl imidazolium][ethyl sulphonate], [1-hexyl-3-methyl imidazolium][tosylate], [1-butyl-3-methyl imidazolium][anthraquinone-2-sulphonate] or [1-butyl-3-methyl imidazolium][5-tert-amyl-naphthoquinone-2-sulphonate]; [tetraalkylammonium][ $Q-(O)-SO_3^-]$  such as any one of [methyl, tri-ethyl ammonium], [5-tert-amyl-naphthoquinone-2-sulphonate], [methyl, di-ethyl, butyl ammonium][anthraquinone-2-sulphonate] or [choline][5-amyl-benzoquinone-2-sulphonate]; or  $[Q-NR_3^+]$ [alkyl sulphonate] such as [5,6,7,8-tetrahydro anthraquinone-2-aminium, N,N,N-(methyl, diethyl)][methylsulphonate]; [tetraalkylphosphonium][dialkylphosphate] such as any of [ethyl tributyl phosphonium][diethyl phosphate], [phenyl triethyl phosphonium][diisobutyl phosphate].

[0039] Not being bound to specific combinations of groups a multitude of combinations are possible, such as any one of [triisobutyl(methyl)phosphonium][tosylate], [tri-hexyl(tetradecyl)phosphonium][bis 2,4,4-trimethylpentyl phosphinate][tetrabutylammonium][methanesulphonate][1-ethyl-3-methyl imidazolium][HFP], [tripentyl sulphonium][dipentyl, benzyl ammonium], [benzoquinone-2-aminium-N,N,N-diethyl, phenyl][5,6,7,8-tetrahydro-9,10-antraquinone-2-sulphonate], [choline][5-ethoxy-1,4-naphthoquinone-6-sulphate], [N-propyl-pyridinium][saccharinate].

[0040] In addition to those mentioned above, also other kinds of commercially available or otherwise known ionic liquids or salts having such properties in combination with a neutral co-solvent may be used.

[0041] It may also be possible to use a salt where at least one of the ions also function as a mediator that is reacted at the cathode to a reduced form and thus participates in the



cyclic process for generation of hydrogen peroxide. In this case the mediator used may partly or fully consist of ions from such a salt. Examples include salts comprising a cation or an anion of a substituted quinone or a nicotinamide derivate such as those mentioned above.

[0042] The use of an at least partially organic salt as described above in the continuous phase of the electrolyte involves the advantages of combining high solubility of organic mediators like quinones with good electric conductivity. Another advantage is the very low flammability allowing reaction with oxygen to be carried out safely at higher oxygen concentrations and higher temperature than would be the case for conventional flammable solvents. It is also easy to separate hydrogen peroxide therefrom, for example by evaporation or extraction, and thereby obtaining hydrogen peroxide either of high purity or in a mixture with a selected compound for further processing, for example water. Another example is a methanol/hydrogen peroxide mixture for use as reagent in an epoxidation reaction. Use of ionic liquids to form a medium suitable for carrying out reactions involving hydrogen peroxide has been disclosed in B. Chhikara et al. in "Oxidation of alcohols with hydrogen peroxide catalyzed by a new imidazolium ion based phosphotungstate complex in ionic liquid", *Journal of Catalysis* 230 (2005, 436-439).

[0043] The at least partially organic continuous liquid phase of the electrolyte may also comprise further components. For example, a neutral co-solvent as earlier mentioned may be present, preferably in an amount from about 0 to about 50 wt %, more preferably from about 1 to about 20 wt %, most preferably from about 5 to about 10 wt %. The continuous liquid phase may further comprise one or more organic or mineral acids like formic acid, acetic acid, sulphuric acid, hydrochloric acid or phosphoric acid. Examples of other optional additives include hydrogen peroxide stabilisers, emulsifiers, corrosion inhibitors, anti-foaming agents, buffers, conductivity enhancers, viscosity reducers, etc. Examples of hydrogen peroxide stabilisers include those commonly used such as phosphoric acid, phosphonic acid based complexing agents, protective colloids like alkali metal stannate and radical scavengers like pyridine carboxylic acids. Examples of phosphonic acid based complexing agents include 1-hydroxyethylidene-1,1-diphosphonic acid, 1-aminoethane-1,1-diphosphonic acid, aminotri(methylenephosphonic acid), ethylene diamine tetra(methylenephosphonic acid), hexamethylene diamine tetra(methylenephosphonic acid), diethylenetriamine penta(methylenephosphonic acid), diethylenetriamine hexa(methylenephosphonic acid), 1-aminoalkane-1,1-diphosphonic acids (such as morpholinomethane diphosphonic acid, N,N-dimethyl aminodimethyl diphosphonic acid, aminomethyl diphosphonic acid), reaction products and salts thereof, preferably sodium salts.

[0044] It is preferred that the at least partially organic liquid phase has a viscosity at operating conditions below about 100 mPas, more preferably below about 30 mPas, and most preferably below about 10 mPas. Furthermore, due to the inherent risks of handling substantially pure hydrogen peroxide, the product recovered is preferably a mixture of hydrogen peroxide with water or low molecular alcohols, for example methanol. The partial pressure at 100° C. of liquid components that do not form part of the product mixture

should preferably be below about 10 kPa, more preferably below about 1 kPa, most preferably below 0.1 kPa.

[0045] The electrochemical cell may comprise a single compartment for the anode and the cathode or be divided and comprising separate anode and cathode compartments, optionally with one or several compartments in-between, for example an electrodialysis stack enabling any known electrodialysis to be performed. The means for separating the compartments may be a non-selective physical barrier, e.g. a porous membrane or diaphragm, or it may be selectively permeable for certain species such as cations or anions. Also a combination of membranes may be used, such as bipolar membranes enabling splitting of water to protons and hydroxide ions. Non-selective barriers may, for example, be made from asbestos, ceramics, glass, polyolefines, PTFE, PVC, etc. Cation selective membranes may, for example, be made from organic polymers such as PTFE, polystyrene, styrene/divinylbenzene or vinylpyridine/divinylbenzene modified with acid groups like sulphonate, carboxylate or phosphonate. Anion selective membranes may, for example, be made from organic polymers such as PTFE, polystyrene, styrene/divinylbenzene or vinylpyridine/divinylbenzene modified with basic groups like quaternary ammonium. A bipolar membranes may comprise an anion permeable membrane and a cation permeable membrane laminated together, optionally with a catalyst layer in-between. Ion selective and bipolar membranes are commercially available, for example under the trademarks Nafion™, Flemium™, Neosepta bipolar®.

[0046] The electrolyte in the cathode compartment, or cell if no separate cathode compartment is present, may contain one, two or more liquid phases. In a single liquid phase system there is only an at least partially organic liquid electrolyte phase, although inorganic species may be included to the extent they are soluble therein. In a system with two liquid phases there is also a predominantly aqueous phase that may be emulsified or simply mixed into the continuous at least partially organic liquid phase. If there are more than a single liquid phase, the components in the electrolyte will be distributed between the phases depending on their solubility properties. In addition to the liquid phase or phases there may also be gas and/or solids present.

[0047] If a single compartment cell is used, the same electrolyte is normally contacting both the anode and the cathode. In order to let electrolytes of different composition contact the anode and the cathode a divided cell can be used. However, this can also be achieved without any physical barrier in the cell by using anolyte and catholyte compositions that form separate liquid phases and optionally using a difference in density to form different layers contacting the anode and cathode, respectively. It is also possible to use differences in wetting properties to form an aqueous layer on a hydrophilic anode surface and an organic layer on a hydrophobic cathode surface. The electrode surfaces may be purposely modified to create the suitable wetting conditions. In order to prevent a thin liquid film from being slowly dissolved it may be advantageous to ensure that the adjacent liquid phase is saturated with the components of the liquid phase making up the film. One way to ensure that is to provide an emulsion of that second phase. Chemically grafting molecules to the surface is another method for controlling the composition near the electrode surface.



[0048] In the electrolyte contacting the anode at least one component is oxidised. There are several possible embodiments that can be chosen by the selection of composition of the electrolyte and the material of the anode.

[0049] In one embodiment suitable for both single compartment and divided cells, water is reacted at the anode to form oxygen and protons. The oxygen and the protons generated may be used in the reaction with the reduced mediator to form hydrogen peroxide. If the cell is divided the anolyte preferably comprises a solution of NaOH or KOH. The pH is preferably above about 7, for example from about 8 to about 14. Preferably the temperature is from about 20 to about 100° C., most preferably about 30 to about 90° C.

[0050] In another embodiment, most suitable for a divided cell, the electrolyte in contact with the anode comprises chloride ions that are reacted at the anode to chlorine. The chlorine formed may be separated as such or hydrolysed in water to form hypochlorous acid which may be further reacted to form chlorate. The anolyte preferably comprises a solution of NaCl or KCl, possibly in combination with the corresponding chlorates, NaClO<sub>3</sub> or KClO<sub>3</sub>. If the pH is below about 4 the predominant product is Cl<sub>2</sub>. At higher pH the Cl<sub>2</sub> formed is hydrolyzed and hypochlorous acid is formed. A pH from about 4 to about 10 in the bulk of the anolyte is preferred for production of alkali metal chlorate such as sodium chlorate, which thus can be produced simultaneously with hydrogen peroxide. Preferably the temperature is from about 20 to about 100° C., most preferably from about 40 to about 90° C.

[0051] In still another embodiment most suitable for a divided cell, sulfuric acid, alkali or ammonium bisulfate or sulfate in the electrolyte is electrolysed at the anode to Caro's acid, peroxosulphuric acid H<sub>2</sub>SO<sub>5</sub>, or peroxydisulfuric acid, H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, or the corresponding peroxo salt. These species can be used as such, for example in bleaching, or be hydrolysed in water to yield hydrogen peroxide and sulfuric acid or the corresponding alkali salt. The anolyte preferably comprises an aqueous solution of the sulfate. The pH depends on the choice of cation, if it is H<sup>+</sup> the pH is preferably below about 3, if it is NH<sub>4</sub><sup>+</sup> the pH is preferable from about 4 to about 9, if it is an alkali metal like Na<sup>+</sup>, the pH may be above about 8.

[0052] In still another embodiment most suitable for a divided cell, a carboxylic acid or a salt thereof is oxidized in presence of water to yield the corresponding peracid and protons. Possible carboxylic acids include formic acid, acetic acids, propionic acid and benzoic acid. The anolyte preferably comprises an aqueous solution of a carboxylic acid, like peracetic acid, at a pH preferably between 3 to 8 or the alkali salt, like potassium or sodium acetate at a pH between 8 and 12.

[0053] In still another embodiment most suitable for a divided cell, methanol or another organic substance like ethanol, formaldehyde natural gas is used in the anolyte, preferably in mixture with water, and is oxidized to yield primarily carbon dioxide and protons. This anode reaction as such is well known and used in direct methanol fuel cells and contributes to lowering the cell voltage and thereby the overall power consumption. The anolyte preferably comprises a mixture of methanol and water and the pH is preferably from about -1 to about 7.

[0054] In still another embodiment most suitable for a divided cell, hydrogen is oxidized at the anode, preferably a gas diffusion electrode, in the presence of water to yield protons that can be transported to the cathode via a cation permeable membrane. Also this reaction is known for fuel cells and contributes to reducing the electrical power needed to drive the overall reactions. The anolyte preferably comprises phosphoric acid and preferably has a pH from about 1 to about 6.

[0055] In still another embodiment a bipolar membrane achieving water splitting is used to separate the anodic and cathodic compartments. The hydroxide formed inside the membrane are transported to the anode compartment, while the protons formed are transported to the cathode compartment where they may react to form hydrogen peroxide or any of the reduced forms of mediator involved, for example hydroquinone or any of the intermediate forms of the mediator. At the anode any reaction, including those mentioned above, may occur, for example with an anolyte comprising any of NaOH, KOH or NH<sub>3</sub> and having a preferred pH from about 8 to about 14 or comprising chloride ions and having a preferred pH from about 5.5 to about 8. One possible reaction is to oxidise hydrogen at a gas diffusion electrode in an anolyte preferably comprising KOH and preferably having a pH from about 8 to about 14.

[0056] Also other anodic reactions are possible within the scope of the invention, such as destruction of various waste products, electrochemical oxidation of white liquor to yield e.g. polysulfides or sulfur dioxide, indirect oxidation of anthracene to anthraquinone or naphthalene to naphthoquinone, e.g. using the redox couples Cr(III)/Cr(VI) or Ce(III)/Ce(IV), or electrolysis of weak black liquor, e.g. to generate oxygen.

[0057] In the cell the temperature and the pressure are preferably set so the electrolyte is liquid. A high temperature favours low viscosity, high electrical conductivity and high mass transfer rates, while a low temperature favours the stability of hydrogen peroxide and components in the electrolyte. Normally the temperature is preferably from about 0 to about 200° C., more preferably from about 40 to about 150° C., most preferably from about 60 to about 100° C. The pressure is preferably from about 10 to about 30000 kPa, more preferably from about 80 to about 2000 kPa, most preferably from about 100 to about 800 kPa. If the cell comprises more than one compartment, the conditions may be the same or different in the various compartments, although it is preferred to operate within the above ranges in all cell compartments.

[0058] The reaction of the one or more reduced forms of the mediator and oxygen to yield hydrogen peroxide may take place inside the cell or in a separate vessel or as a combination of the two, resulting in formation of hydrogen peroxide in the at least partially organic phase of the electrolyte and reformation of the mediator to take part in another reaction cycle. Normally molecular oxygen is added to the electrolyte comprising reduced mediator, but part of it may come from oxygen generated in anodic reactions and transported through the electrolyte in the cell, optionally via a membrane, or be isolated as a separate stream and reintroduced into the cell. Molecular oxygen may be added dissolved in a liquid or in the form of any oxygen containing gas such as air, oxygen enriched air or substantially pure



oxygen. Adding at least part of the oxygen as a gas directly into the cell involves the advantage of improving the agitation and may also create a gas-lift for transporting electrolyte out of cell, alternatively contribute to stripping of hydrogen peroxide from the electrolyte. Adding oxygen directly to the cell may enable the full catalytic cycle of the mediator to be completed inside the cell, substantially eliminating the need for withdrawing a stream comprising a reduced form of the mediator and feeding a stream comprising a mediator. The reactions to yield hydrogen peroxide are facilitated by the presence of protons that may originate from any available source, such as water, hydroquinone, protons generated at the anode or any acid that has been added to the electrolyte. If the reaction with oxygen takes place in a separate vessel, the conditions like temperature, pressure etc. may be the same or different from what is prevailing in the cell. The temperature is preferably from ambient, e.g. about 20° C., to an upper limit determined either by the flammability of the solvent or the stability of the hydrogen peroxide, for example up to about 70° C. The pressure is preferably from about atmospheric up to about 5 barg. Generally it is preferred to use a bubble column, either packed or with sieve plates. Preferably oxygen containing gas is fed at the bottom and the liquid flows either upwards or downwards.

[0059] Various methods may be used for separating hydrogen peroxide from the electrolyte, such as evaporation, extraction or membrane-based technologies. The separation may take place in the cell, in separate equipment from which the remaining electrolyte then is recycled back to the cell, or a combination thereof.

[0060] In one embodiment hydrogen peroxide is evaporated from the at least partially organic phase of the electrolyte, preferably together with water and optionally other volatile substances that might be present. The evaporation may be effected directly from the cell or from a separate vessel, for example, by stripping with any gas, e.g. oxygen, air or nitrogen, or by distillation at atmospheric or sub-atmospheric pressure. A low vapour pressure of the at least partially organic salt and other organic species optionally present in the electrolyte and not forming part of the desired product mixture facilitates the use of evaporation techniques for separating hydrogen peroxide. In this embodiment is possible to obtain a hydrogen peroxide containing product stream of high purity without extensive purification steps.

[0061] In another embodiment hydrogen peroxide is extracted from the at least partially organic liquid phase by any suitable solvent such as water or methanol. All commonly used extraction technologies may be used, such as one or several mixer-settlers, sieve-plate columns, packed bed columns. If an electrolyte also comprising a predominantly aqueous phase is used, hydrogen peroxide will automatically be enriched in that phase, which may be withdrawn as a product, alternatively be subjected to distillation or other kind of purification and recycled back to the cell.

[0062] In a further embodiment membrane based separation is used. Examples of such processes include membrane extraction, pervaporation and nanofiltration.

[0063] In still a further embodiment hydrogen peroxide is not withdrawn from the electrolyte but is used directly as a reactant in the production of other chemicals. Electrolyte remaining after such reactions may then be recycled to the cell.

[0064] The process is preferably operated continuously, either with electrolyte flowing through the cell or by continuously separating hydrogen peroxide from the electrolyte in the cell. It is preferred to serve for adequate agitation, particularly around the cathode, for example by gas blow, mechanical agitation, circulation of electrolyte, or combinations thereof. Gas blow is preferably done with oxygen or oxygen containing gas such as air. In a cell with an essentially vertical flow, gas blowing may also create a gas-lift enhancing the transport of electrolyte through the cell alternatively stripping of hydrogen peroxide, optionally together with water or any other component that is volatile at the temperature and pressure of operation.

[0065] In order to avoid detrimental accumulation of impurities from feed chemicals or degradation products formed in side reactions it may in some cases be advisable to bleed off part of the electrolyte from the system and/or purifying with various methods like electrodialysis, adsorption, recrystallization, precipitation, washing, ion-exchange, evaporation or stripping using a carrier gas, reactive regeneration with acid/base or reductive/oxidative steps.

[0066] As hydrogen gas may be formed as a side reaction on the cathode it may be appropriate to include a gas analyzer and a device for flushing with inert gas.

[0067] The temperature may be controlled by any suitable means, e.g. by heat exchangers at any appropriate flow. Cooling can also be effected by evaporation, e.g. in the electrochemical cell, and subsequent condensation of the vapour. If evaporative cooling is effected by water it may be appropriate to add water specifically for this purpose.

[0068] Various kinds of cathodes may be used. It is preferred that the cathode is made of a material suppressing parasitic reactions like hydrogen evolution, direct oxygen reduction to water and destruction of the organic mediator, the ionic liquid or the hydrogen peroxide formed. In most cases it is preferred to use a cathode with a hydrophobic surface. Examples of materials for the cathode include carbon based materials like boron doped diamond, graphite, glassy carbon, highly oriented pyrolytic graphite, reticulated carbon and conductive polymers. Examples of conductive polymers include poly(para)phenylene, polypyrrole, polythiophene and polyaniline. The conductive polymer can be applied as a thin film, with a preferred thickness from about 0.1 to about 100  $\mu\text{m}$ , on any suitable substrate, such as Pt or stainless steel. The polymer film can be prepared by chemical synthesis or preferably by electrosynthesis. A specific example is a cathode obtained electrosynthesis of a polypyrrole film on stainless steel. Other examples cathode materials include metals like iron, steel, lead, nickel, titanium or platinum, or conductive metal oxides such as  $\text{PbO}_2$ ,  $\text{NiO}_2$ ,  $\text{Ti}_4\text{O}_7$ ,  $\text{NiCO}_2\text{O}_4$  or  $\text{RuO}_2$ . Still further examples include electrocatalytic cathodes of a material like titanium or titanium alloy coated, fully or partially, with particles of noble metals like gold, platinum, palladium or grafted with catalysts for anthraquinones.

[0069] Also the anode may be made from many kinds of material. Although many metals as such are not thermodynamically stable, oxides of e.g. platinum, lead, nickel, titanium, tantalum and niobium are useful. Also graphite and electrocatalytic anodes like DSA (dimensionally stable anode) can be used, preferably obtained by coating a material like titanium or a titanium alloy with catalytic metals and/or metal oxides.



[0070] For water oxidation at high pH, preferably from about 8 to about 15, preferred materials are steel or nickel coated with high surface area deposits of nickel or other catalytic metal, like platinum, or mixed oxides of spinell or perovskite type. For water oxidation at low pH, preferably from about -1 to about 7, DSA anodes are preferred, for example titanium or a titanium alloy coated with  $\text{Ta}_2\text{O}_5/\text{IrO}_2$ .

[0071] For chloride oxidation DSA anodes are preferred, such as titanium or titanium alloy coated with e.g.  $\text{RuO}_2/\text{TiO}_2$ ,  $\text{RuO}_2/\text{TiO}_2/\text{IrO}_2$  or  $\text{Pr}/\text{Ir}$ .

[0072] For sulfate and bisulfate oxidation preferred materials are Pt, Pt/Ta/Ag and  $\text{PbO}_2$ .

[0073] For oxidation of carboxylic acids to percarboxylic acids preferred materials are Pt, Au or Carbon.

[0074] For methanol oxidation preferred materials are mixed oxides of spinell or perovskite type, optionally containing any of Pt and Ru.

[0075] For hydrogen oxidation preferred materials are PTFE bonded carbon in combination with one or more noble metals, carbon or graphite felt coated with one or more noble metals, or mixed oxides of spinell or perovskite type.

[0076] The cathode and the anode can be made in various geometrical shapes and may, for example, take the form of a flat sheet or plate, a curved surface, a convoluted surface, a punched plate, a woven wire screen, an expanded mesh sheet, a rod, or a tube. However, the anode and cathode preferably have a planar shape, most preferably in the form of a sheet, mesh or plate.

[0077] Any conventional cell design can be used, preferably with as short distance as possible between the anode and cathode. A divided cell may, for example, be of the "zero gap" type where at least one of the electrodes is pressed against a membrane dividing the cell.

[0078] A typical production plant includes a multitude of cells to achieve the desired production rate. The cells can be arranged in a monopolar or bipolar way in an electrolyser according to any conventional design.

[0079] Some embodiments of the invention will now be further described in connection with the appended schematic drawings. However, the scope of the invention is not limited to these embodiments. FIG. 1 shows a schematic configuration of the cathodic process part, while FIGS. 2, 3 and 4 show schematic designs of various electrochemical cells.

[0080] Referring to FIG. 1, an electrochemical reduction of the mediator takes place in an at least partially organic continuous phase of an electrolyte in a cell compartment 1, that may be a cathode compartment or a single compartment cell. A feed stream 14 provides the cell compartment 1 with any substances that are consumed in the process, such as oxygen, or withdrawn in any product stream not recycled, such as water or an inert gas like nitrogen. If oxygen is present a reaction between the reduced form or forms of the mediator and oxygen to hydrogen peroxide or alkali metal peroxide may also take place in the cell compartment 1. If this reaction proceeds to a sufficiently large extent it is sufficient to remove the hydrogen peroxide together with e.g. water in a stream 6. If the reaction to hydrogen peroxide or alkali metal peroxide is incomplete electrolyte is with-

drawn and the reaction completed to the extent desired in an oxidation reactor 2 where additional oxygen 15 may be supplied. A resulting stream 7 contains hydrogen peroxide or an alkali metal peroxide in one or several forms depending on the conditions used, for example as a vapour or dissolved in a liquid phase. If both a gas and at least one liquid phase is present they are brought to a gas liquid separator 3 from which a gas stream 8 is brought to a condenser 4. Hydrogen peroxide product 10 is withdrawn from the condenser 4 while remaining gas 13, e.g. oxygen, steam and other optional components, is either recycled to any point where oxygen can be used, such as the cell compartment 1 or the oxidation reactor 2, or bleed off via 16. A liquid stream 9 from the separator 3 is recycled to the cell compartment 1. If the liquid stream 9 contains hydrogen peroxide it is first brought to a separator 5, which, for example, may be an extraction unit or a membrane separation unit. Here the stream 5 is separated into a hydrogen peroxide containing product stream 11 and a recycle stream 12 comprising the at least partially organic electrolyte.

[0081] The various units illustrated in FIG. 1 can be combined in a multitude of ways. For example, oxygen may be introduced in the cell compartment 1 in various ways, for example separately or together with any liquid feed or recycled stream. Oxygen may also be introduced at a position above the electrodes in order to separate the electrochemical reactions and the oxidation. The oxidation reactor 2 and the gas liquid separator 3 may be combined, for example by using a bubble column. If the operation conditions are set so no gas forms and only a liquid phase is withdrawn from the cell compartment 1, the gas liquid separator 3 and the condenser 4 may be omitted.

[0082] Referring to FIG. 2, an electrochemical cell operated according to the invention comprises an anode 21 in an anode compartment 23 and a cathode 22 in a cathode compartment 24. The cell also comprises a middle compartment 25 separated from the anode and cathode compartments 23, 24 by ion selective membranes 26, 27. In one embodiment, the membrane 26 is anion permeable and the membrane 27 is cation permeable. In another embodiment both membranes 26, 27 are cation permeable. The cathode compartment 24 holds a catholyte comprising an organic mediator according to the invention. Oxygen containing gas is fed through inlet stream 28 to the cathode compartment 24 and an outlet stream 29 comprising hydrogen peroxide and/or reduced mediator is brought to a unit 30 where further processing takes place. Such further processing may include oxidation of reduced mediator to obtain hydrogen peroxide and separation thereof, resulting in a product stream 31 comprising hydrogen peroxide and optionally other species, such as water that may remain in the final product and others that may be separated later, and a recycle stream 32 comprising e.g. catholyte with an organic mediator obtained by oxidation of the reduced forms thereof. The anode compartment 23 is fed with an inlet stream 33 that may have various compositions depending on the desired reactions. Anolyte, including reaction products, are withdrawn in an outlet stream 34 to a product separator 35 from which a product 36 is withdrawn and remaining electrolyte 37 recycled to the anode compartment 23. The middle compartment 25 is fed through an inlet stream 38 with a preferably aqueous solution, the composition of which depends on the desired overall reactions. An outlet stream 39 from the middle compartment 25 may be recycled or used in any other way.



[0083] If the cell of FIG. 2 is used in an embodiment where both the membranes 26, 27 are cation selective and water is reacted at the anode 21 to form oxygen and protons, the anolyte is preferably composed of water and a suitable electrolyte, such as KOH or NaOH. Oxygen is withdrawn together with anolyte through outlet stream 34 and is separated therefrom in separator 35. Remaining anolyte 37 is recirculated to the anode compartment 23 while the oxygen may be transferred to the cathode compartment 24 or a separate unit for oxidation of reduced mediator to form hydrogen peroxide. Protons from the anolyte are transferred to the middle compartment 25 through the cation selective membrane 26. The middle compartment 25 is preferably fed through the inlet stream 38 with a preferably aqueous solution containing protons or cations like sodium ions that can be transferred through the cation selective membrane 27 to the cathode compartment 24. Examples of such solutions are solvents like water containing  $\text{HCl}$ ,  $\text{H}_x\text{PO}_3^{(3-x)-}$ ,  $\text{H}_x\text{SO}_4^{(2-x)-}$ ,  $\text{NaClO}_3$  or acetic acid.

[0084] If the cell of FIG. 2 is used in an embodiment where the membrane 26 is anion selective, the membrane 27 is cation selective and chloride is reacted at the anode to form chlorine that may be hydrolysed further to form chlorate, the anolyte is preferably an aqueous solution comprising  $\text{NaCl}$ ,  $\text{NaClO}_3$ , or the corresponding potassium salts  $\text{KCl}$  or  $\text{KClO}_3$ , and optionally a buffer such as chromate, dichromate or any other suitable salt. A product stream 34 of anolyte is withdrawn and brought to product separator 35 where alkali metal chlorate is crystallised and withdrawn 36 while remaining electrolyte is recycled 37 to the anode compartment 23. It is also possible to provide a unit (not shown) for further reactions to form chlorate in the withdrawn product stream 34 before the crystallisation. In one option the middle compartment 39 is preferably fed through inlet stream 38 with a solvent like water containing  $\text{HCl}$  or  $\text{NaCl}$  and chloride ions are transferred through the anion selective membrane 26 to the anode compartment 23 where they are consumed at the anode 21 to form chlorine in a first step. Then  $\text{Na}^+$  or  $\text{K}^+$  are fed to the cathode compartment 23 through inlet stream 33 for example in the form of  $\text{NaOH}$  or  $\text{KOH}$ . In another option the middle compartment 25 is fed through inlet stream 38 with  $\text{OH}^-$ , for example as  $\text{NaOH}$  or  $\text{KOH}$ , the hydroxide ions will be transferred through the anion selective membrane 26 and chloride ions are then fed through inlet stream 33, for example as  $\text{NaCl}$ . In either option cations, normally  $\text{Na}^+$  or  $\text{H}^+$ , are transferred from the middle compartment 25 through the cation selective membrane 27 into the cathode compartment 24.

[0085] Referring to FIG. 3, an electrochemical cell operated according to the invention comprises an anode 21 in an anode compartment 23 and a cathode 22 in a cathode compartment 24. However, in contrast to the cell of FIG. 2 there is only one ion selective membrane 27, which preferably is cation selective, and there is no middle compartment. In all other aspects the cell is identical to the one of FIG. 2, the description of which is referred to.

[0086] If the cell in FIG. 3 is provided with a cation selective membrane 27 and is used in an embodiment where chloride reacts at the anode 21 to form chlorine that is hydrolyzed further to form chlorate, the anolyte is preferably an aqueous solution comprising  $\text{NaCl}$ ,  $\text{NaClO}_3$ , or the corresponding potassium salts  $\text{KCl}$  or  $\text{KClO}_3$ , and a buffer such as chromate or any other suitable salt.  $\text{NaCl}$  or  $\text{KCl}$  is

fed to the anode compartment 23 through inlet stream 33 while cations such as  $\text{Na}^+$  or  $\text{H}^+$  are transferred through the membrane 27 into the cathode compartment 24. In order to compensate for loss of  $\text{Na}^+$  or  $\text{K}^+$  through the membrane 27 and neutralising  $\text{H}^+$  formed in the anodic reactions it may be appropriate to add some  $\text{NaOH}$  or  $\text{KOH}$  at any suitable position, e.g. to the inlet stream 33 or the recycle stream 37. In all other aspects, like the handling of product 34 and recycle streams 37, the operation is equivalent to the corresponding embodiment performed in the cell of FIG. 2, the description of which is referred to.

[0087] If the cell in FIG. 3 is provided with a cation selective membrane 27 and is used in an embodiment for destruction of waste products such as  $\text{SO}_2$ , this is fed to the anode compartment together with water through stream 33 and oxidised at the anode 21 to form sulfuric acid dissolving into the water and withdrawn through product stream 34. Any protons or other cations present pass through the membrane 27 into the cathode compartment 24.

[0088] If the cell in FIG. 3 is provided with a cation selective membrane 27 and used in an embodiment where hydrogen is oxidised to protons on a gas diffusion anode 21 provided with a catalyst, protons are transferred through the membrane 27 into the cathode compartment 24 and facilitates the formation of hydrogen peroxide. The anolyte, e.g. comprising phosphoric acid, may circulate through the anode compartment 23 without withdrawing any product and the separation unit 35 may then be omitted.

[0089] Referring to FIG. 4 an electrochemical cell operated according to the invention comprises an anode 21 in an anode compartment 23 and a cathode 22 in a cathode compartment 24. However, in contrast to the cell of FIG. 2, the middle compartment is replaced by a bipolar membrane 40 separating the cell compartments 23, 24. The bipolar membrane 40 comprises an anion selective membrane 26 and a cation selective membrane 27 laminated together on each side of a catalyst layer 45. Water from the anolyte pass into the catalyst layer where it is split to protons passing into the cathode compartment 24 and hydroxide ions passing into the anode compartment 23. In all other aspects the cell is identical to those of FIGS. 2 and 3, the descriptions of which are referred to.

[0090] If the cell of FIG. 4 is used in an embodiment where water is reacted at the anode 21 to form oxygen and protons, the anolyte is preferably composed of water and a suitable electrolyte, such as  $\text{NaOH}$  or  $\text{KOH}$  and oxygen is withdrawn together with anolyte through outlet stream 34. Inside the bipolar membrane water is split into protons and hydroxide ions. The protons move into the cathode compartment 24 and facilitates the oxidation of reduced mediator to form hydrogen peroxide, while the hydroxide ions move into the anode compartment 23 and are neutralised by the protons from the anodic reactions. In all other aspects, like the handling of product 34 and recycle streams 37, the operation is equivalent to the corresponding embodiment performed in the cell of FIG. 2, the description of which is referred to.

[0091] If the cell of FIG. 4 is used in an embodiment where chloride reacts at the anode 21 to form chlorine that is reacted further to form chlorate, the anolyte is preferably an aqueous solution comprising  $\text{NaCl}$ ,  $\text{NaClO}_3$ , or the corresponding potassium salts  $\text{KCl}$  or  $\text{KClO}_3$ , and a buffer



such as chromate or any other suitable salt. NaCl or KCl is fed to the anode compartment **23** through inlet stream **33**. Inside the bipolar membrane water is split into protons and hydroxide ions. The protons move into the cathode compartment **24** and facilitates the oxidation of reduced mediator to form hydrogen peroxide, while the hydroxide ions move into the anode compartment **23** facilitating the hydrolysis of chlorine. In all other aspects, like the handling of product **34** and recycle streams **37**, the operation is equivalent to the corresponding embodiments performed in the cell of FIG. 2, the description of which is referred to.

[0092] In all the embodiments described in FIGS. 2-4 the cathodic process may be the same, i.e. reduction of the mediator at the cathode **22** and transfer of cations like  $H^+$  or  $Na^+$  from the middle compartment **25** or the anode compartment **23** through the cation selective membrane **27**. If oxygen is formed and withdrawn from the anode compartment **23** it may be transferred to the cathode compartment **24** or to a separate unit for oxidation of the reduced form of the mediator formed in the cathode compartment **24**.

[0093] The invention will now be further described through the following examples. If not otherwise stated, all parts and percentages refer to parts and percent by weight.

#### EXAMPLE 1

[0094] A solution containing 25 ml of the ionic liquid 1-butyl-3-methyl-imidazolium hexafluorophosphate [BMIM][HFP] with 0.1 g 2-ethyl-9,10-anthraquinone (EAQ) as mediator was poured into a small reactor and heated to 60° C. Nitrogen gas saturated with water was purged into the solution for 30 minutes to dissolve gases in the solution and to saturate the solution with water. On top of the organic phase an aqueous phase containing 0.05 M  $H_2SO_4$  was added to supply protons. A cathode of circular platinum mesh with a diameter of 3 cm was placed in the organic phase and a platinum mesh anode was placed in a separate compartment containing 10 mM NaOH aqueous solution. The anode and cathode compartments were separated with a non-selective ceramic membrane (diaphragm). The catholyte was stirred by a magnetic bar located in the organic phase in the cathode compartment. To keep track of the cathodic potential a reference electrode (Metrohm 6.0726.110 Ag/AgCl) was placed in the cathode compartment close to the cathode.

[0095] As a first test a current of around 30 mA was applied through the cell for 10 minutes, which gave an increasing potential at around 1 V vs. ref. In the anode compartment oxygen was formed. The cathode became reddish in colour, which was suspected to be a complex of a reduced form of EAQ. After this the hydrogen peroxide concentration was measured, which gave zero mg/l. Oxygen was then purged through the solution and a hydrogen peroxide concentration of 5 mg/l was observed in the water phase in the cathode compartment.

[0096] From these results it can be concluded that oxygen was not reduced at the cathode to form hydrogen peroxide, instead it must have been EAQ that was first reduced and then reacted with oxygen to form hydrogen peroxide.

#### EXAMPLE 2

[0097] In a similar setup as in Example 1 a two phase system was used as catholyte, a lower phase of 50 ml

[BMIM][HFP] with 0.8 g EAQ dissolved therein and an upper phase of 40 ml 0.5 M  $H_2SO_4$  solution. A cathode of steel mesh with an area of about 13 cm<sup>2</sup> was located in the lower phase while oxygen was continuously bubbled into the upper phase. An anode compartment with 10 mM NaOH as described in Example 1 was immersed into the solution. At a temperature of 68° C. a current of 0.2 A was placed between the anode and cathode for 30 minutes, which created an almost black solution due to the reduced EAQ. The hydrogen peroxide was then measured in the water phase and used as a basis for calculating a current efficiency for hydrogen peroxide formation was 22% (i.e. not including hydrogen peroxide remaining in the phase of [BMIM][HFP]).

#### EXAMPLE 3

[0098] The same set-up and conditions as in Example 1 was used except that the acid in the aqueous phase in the cathode compartment was changed to 2 wt % phosphorous acid and a Calomel reference electrode was used instead of Ag/AgCl. A current was applied between the anode and cathode and a build-up of hydrogen peroxide was observed. After 100 minutes the hydrogen peroxide concentration in the aqueous phase was measured and found to be around 250 mg/l.

#### EXAMPLE 4

[0099] The same set-up and conditions as in Example 2 was used with the exception that the anode compartment contained an aqueous solution of 150 g/l NaCl and 10 g/l sodium dichromate. During the experiment a few droplets of NaOH (1M) was added to the anolyte to keep the pH between 6 and 7. In the cathode compartment hydrogen peroxide was formed as described in the Example 2. In the anode compartment chloride was oxidized to chlorine which eventually formed chlorate. After 20 minutes the experiment was terminated and a current efficiency for chlorate formation was calculated to 59%.

1. Process for the production of hydrogen peroxide comprising:

providing an electrochemical cell comprising an anode and a cathode;

contacting the cathode with an electrolyte comprising at least one organic mediator dissolved in an at least partially organic continuous liquid phase comprising an at least partially organic salt and a neutral co-solvent, said salt comprising at least one kind of organic cation and/or organic anion, said continuous liquid phase having an electrical conductivity under process conditions of at least about 0.1 S/m;

reacting the organic mediator at the cathode to form at least one reduced form of the mediator; and,

reacting the at least one reduced form of the mediator with oxygen to form hydrogen peroxide.

2. Process as claimed in claim 1, wherein a neutral co-solvent is present in the at least partially organic continuous liquid phase of the electrolyte in an amount up to about 50 wt %.



3. Process as claimed in claim 2, wherein a neutral co-solvent is present in the at least partially organic continuous liquid phase of the electrolyte in an amount from about 1 to about 20 wt %.

4. Process as claimed in claim 1, wherein the co-solvent is water.

5. Process as claimed in claim 1, wherein the organic mediator is selected from the group consisting of quinones, flavoquinones, pyridine derivatives, and ketones.

6. Process as claimed in claim 5, wherein the organic mediator is selected from the group consisting of quinones containing a (benzo)quinone-moiety.

7. Process as claimed in claim 6, wherein the organic mediator is selected from the group consisting of anthraquinones, tetrahydro anthraquinones, naphthoquinones, benzoquinones and derivatives thereof.

8. Process as claimed in claim 1, wherein the content of organic mediator, including the reduced forms, in the at least partially organic continuous liquid phase is at least about 1 wt %.

9. Process as claimed in claim 1, wherein the content of the at least partially organic salt in the continuous liquid phase is from about 20 wt % to about 99 wt %.

10. Process as claimed in claim 1, wherein the at least partially organic salt that in itself or in combination with a neutral co-solvent forms a liquid phase at atmospheric pressure below about 130° C.

11. Process as claimed in claim 1, wherein the at least partially organic salt at 100° C. has a partial pressure below about 10 kPa.

12. Process as claimed in claim 1, wherein the at least partially organic salt comprises a cation selected from the group consisting of 1-alkyl-3-methyl imidazolium, 1-butyl-3-methyl imidazolium [BMIM], 1-ethyl-3-methyl imidazolium [EMIM], 1,2,3-trimethyl imidazolium, N-alkylpyridinium, N-butyl pyridinium [BPY], pyrrolidinium, guanidinium and alkyl guanidinium, isouronium,  $PR_4^+$ ,  $NR_4^+$ ,  $SR_3^+$ , tetramethylammonium, choline, cocomonium, and mixtures thereof, R being, independently of each other, optionally substituted alkyl, alkenyl or aryl, or hydrogen.

13. Process as claimed in claim 1, wherein the at least partially organic salt comprises a cation selected from the group consisting of substituted quinones.

14. Process as claimed in any claim 1, wherein the at least partially organic salt comprises an anion selected from the group consisting of hexafluorophosphate [HFP], tetrafluoroborate [TfB], fluorosulfonate, hexafluoroantimonate, hexafluoroarsenate, chloroaluminate, bromoaluminate, bis-(trifluoromethylsulfonyl)imide, tris(trifluoromethylsulfonyl)methide, tricyanomethide, dicyanamide, nonafluorobu-

tanefluoroborate, trifluoromethane sulfonate, 2,2,2-trifluoroethanesulfonate, nitrate, sulphate, phosphate,  $RPO_4^{2-}$ ,  $R_2PO_4^-$ ,  $R_2PO_2^-$  (e.g. a dialkylphosphinate), perchlorate, acetate, alkylsulphonate, bis(2-ethylhexyl)sodium sulfosuccinate, diethyleneglycolmonomethylethersulfate, alkyloligoethersulfate, pivalate, tetraalkylborate, propionate, succinate, saccharinate, glycolate, stearate, lactate, malate, tartrate, citrate, ascorbate, glutamate, benzoate, salicylate, methanesulfonate, toluenesulfonate, and mixtures thereof, R being, independently of each other, optionally substituted alkyl, alkenyl or aryl, or hydrogen.

15. Process as claimed in any claim 1, wherein the at least partially organic salt comprises an anion selected from the group consisting of substituted quinones.

16. Process as claimed in claim 1, wherein the at least partially organic salt comprises a cation selected from the group consisting of [1,3-dialkyl imidazolium], [trialkylammonium], [tetraalkylammonium], [trialkylphosphonium], [tetraalkylphosphonium], [alkylpyridinium], [choline],  $[Q-NR_3^+]$  and  $[Q-PR_3^+]$  and an anion selected from the group consisting of [sulphate], [phosphate], [alkyl sulphate], [alkyl sulphonate], [dialkyl phosphate], [alkyl phosphonate],  $[Q-(O)-SO_3^-]$  and  $[Q-(O)-PO_3R^-]$ , where Q is a quinone, (O) is an optional oxygen and R is, independently of each other, optionally substituted alkyl, alkenyl or aryl, or hydrogen.

17. Process as claimed in claim 1, wherein the electrochemical cell comprises separate anode and cathode compartment.

18. Process as claimed in any one of the claims 1-17, wherein the electrolyte in the cathode compartment, or cell if no separate cathode compartment is present, contains a single liquid phase.

19. Process as claimed in claim 1, wherein molecular oxygen is added to the at least partially organic phase of the electrolyte comprising reduced mediator, resulting in formation of hydrogen peroxide in the electrolyte.

20. Process as claimed in claim 19, wherein at least part of the oxygen is added to the at least partially organic phase of the electrolyte comprising reduced mediator as a gas directly into the electrochemical cell.

21. Process as claimed in claim 1, wherein hydrogen peroxide is evaporated from the at least partially organic phase of the electrolyte.

22. Process as claimed in claim 1, wherein hydrogen peroxide is extracted from the at least partially organic liquid phase.

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