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FOR THE PRODUCTION OF ALKALI
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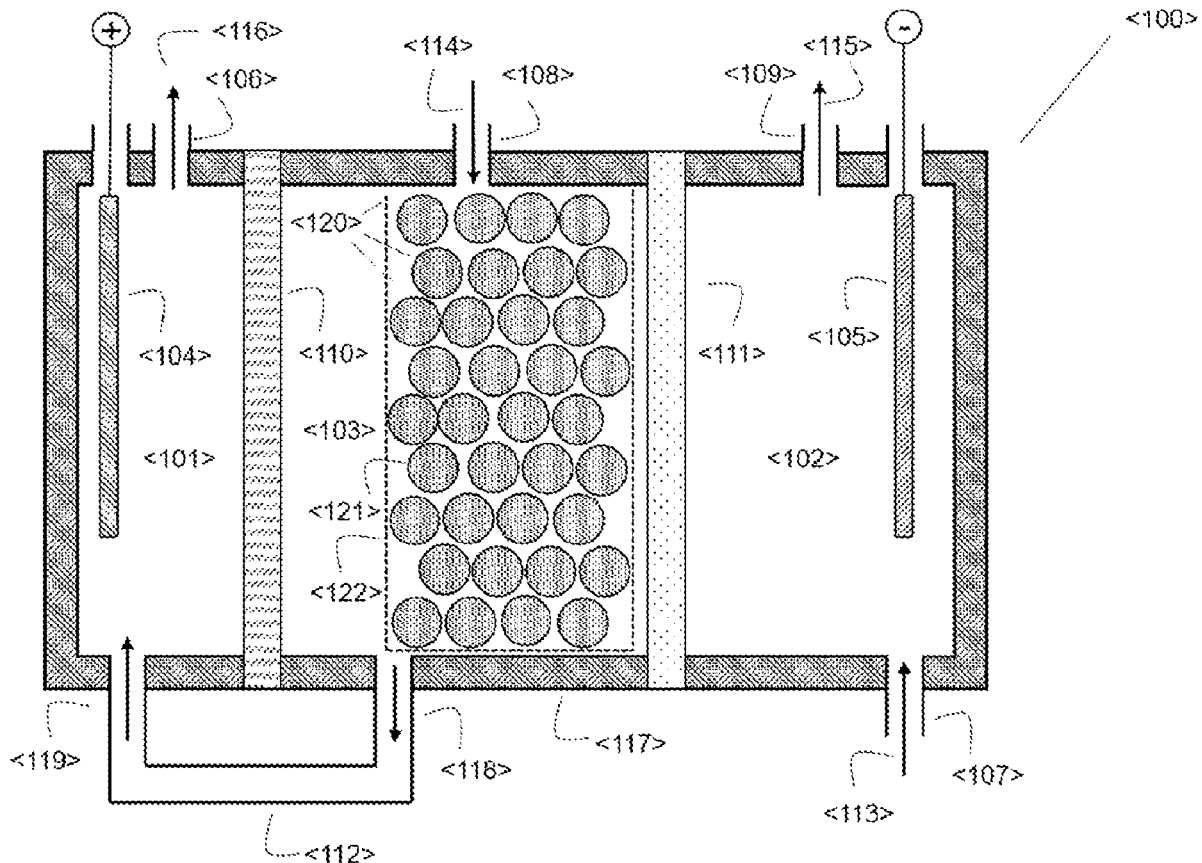
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ABSTRACT

The present invention relates, in a first aspect, to an electrolysis cell having three chambers, wherein the middle chamber is separated from the cathode chamber by a solid-state electrolyte permeable to cations, for example NaSi-CON, and from the anode chamber by a diffusion barrier. The invention is characterized in that the middle chamber comprises internals.

The electrolysis cell according to the invention solves the problem that a concentration gradient forms in the middle chamber of the electrolysis cell during the electrolysis, which leads to locally lowered pH values and hence to damage to the solid-state electrolyte. The internals result in vortexing of the electrolyte solution as it flows through the middle chamber during the electrolysis, which prevents the formation of a pH gradient.

In a second aspect, the present invention relates to a process for producing an alkali metal alkoxide solution in the electrolysis cell according to the invention.



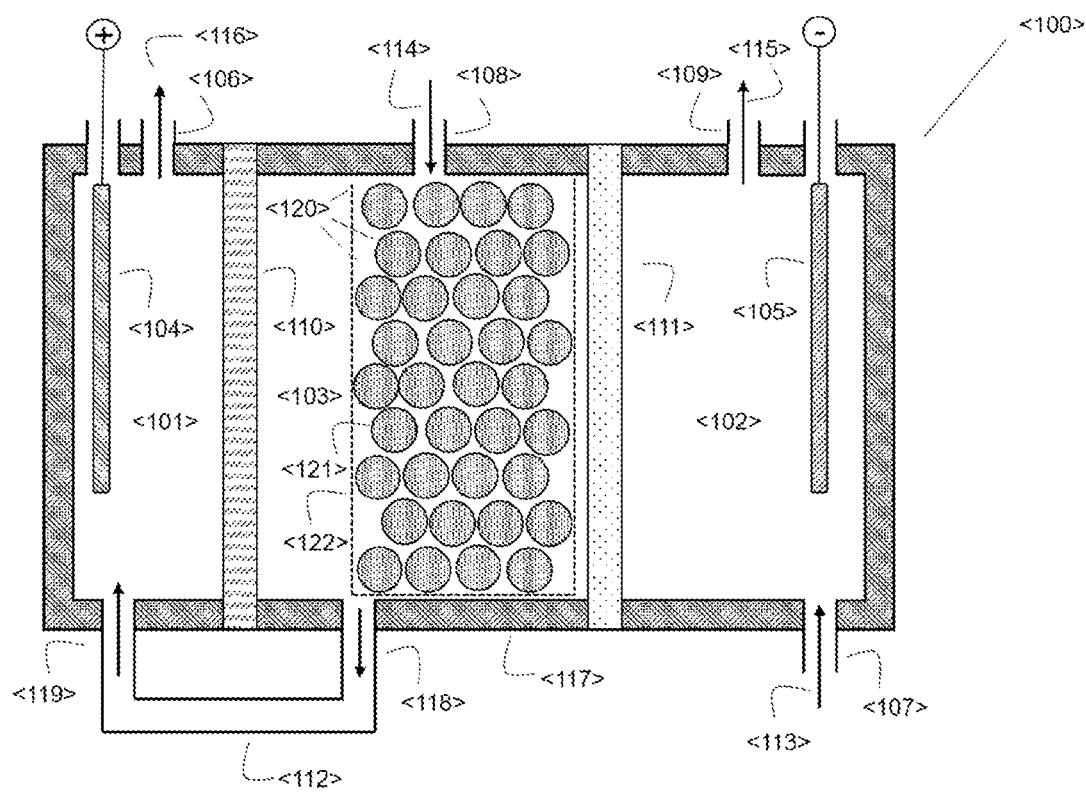


Figure 1

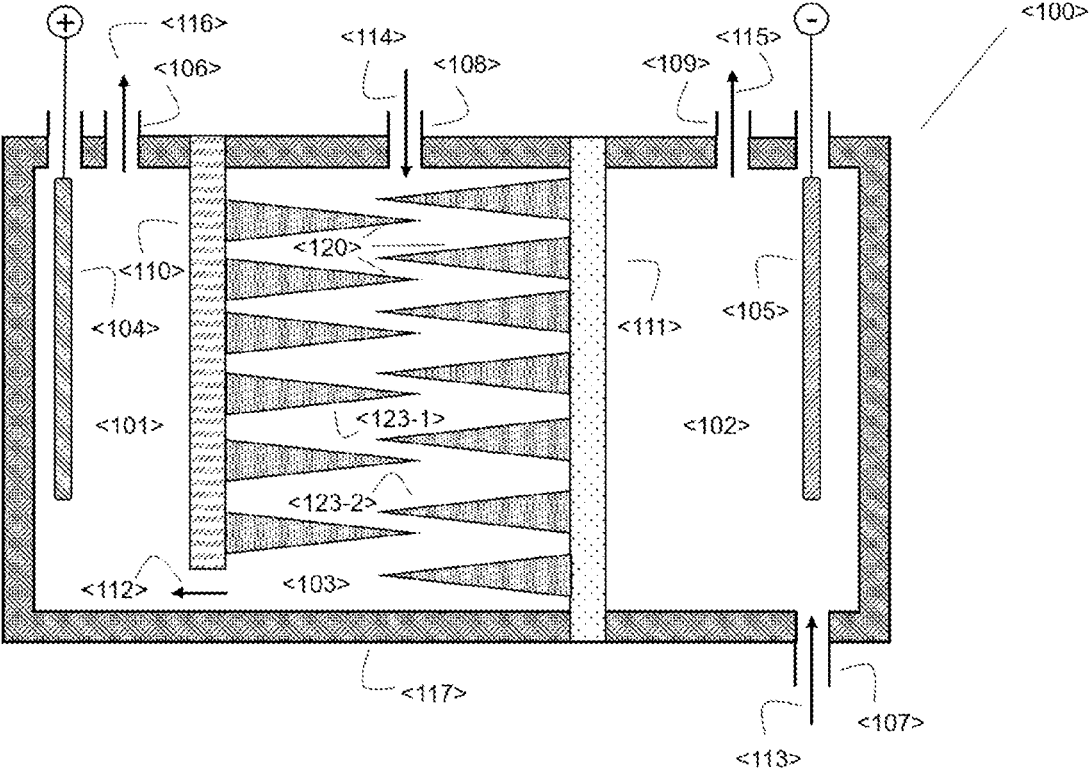


Figure 2

THREE-CHAMBER ELECTROLYTIC CELL FOR THE PRODUCTION OF ALKALI METAL ALKOXIDES

[0001] The present invention relates, in a first aspect, to an electrolysis cell having three chambers, wherein the middle chamber is separated from the cathode chamber by a solid-state electrolyte permeable to cations, for example NaSICON, and from the anode chamber by a diffusion barrier. The invention is characterized in that the middle chamber comprises internals.

[0002] The electrolysis cell according to the invention solves the problem that a concentration gradient forms in the middle chamber of the electrolysis cell during the electrolysis, which leads to locally lowered pH values and hence to damage to the solid-state electrolyte. The internals result in vortexing of the electrolyte solution as it flows through the middle chamber during the electrolysis, which prevents the formation of a pH gradient.

[0003] In a second aspect, the present invention relates to a process for producing an alkali metal alkoxide solution in the electrolysis cell according to the invention.

1. BACKGROUND OF THE INVENTION

[0004] The electrochemical production of alkali metal alkoxide solutions is an important industrial process which is described, for example, in DE 103 60 758 A1, US 2006/0226022 A1 and WO 2005/059205 A1. The principle of these processes is reflected in an electrolysis cell in which the solution of an alkali metal salt, for example sodium chloride or NaOH, is present in the anode chamber, and the alcohol in question or an alcoholic solution with a low concentration of the alkali metal alkoxide in question, for example sodium methoxide or sodium ethoxide, is present in the cathode chamber. The cathode chamber and the anode chamber are separated by a ceramic that conducts the alkali metal ion used, for example NaSICON or an analogue for potassium or lithium. On application of a current, chlorine forms at the anode—when a chloride salt of the alkali metal is used—and hydrogen and alkoxide ions at the cathode. The charge is balanced in that alkali metal ions migrate from the middle chamber into the cathode chamber via the ceramic that is selective therefor. The balancing of charge between middle chamber and anode chamber results from the migration of cations when cation exchange membranes are used or the migration of anions when anion exchange membranes are used, or from migration of both ion types when non-specific diffusion barriers are used. This increases the concentration of the alkali metal alkoxide in the cathode chamber, and the concentration of the sodium ions in the anolyte is lowered.

[0005] NaSICON solid-state electrolytes are also used in the electrochemical production of other compounds:

[0006] WO 2014/008410 A1 describes an electrolytic process for producing elemental titanium or rare earths. The basis of this process is that titanium chloride is formed from TiO_2 and the corresponding acid, and this is reacted with sodium alkoxide to give titanium alkoxide and NaCl and finally converted electrolytically to elemental titanium and sodium alkoxide.

[0007] WO 2007/082092 A2 and WO 2009/059315 A1 describe processes for producing biodiesel, in which, with the aid of alkoxides produced electrolytically by means of NaSICON, triglycerides are first converted to the corre-

sponding alkali metal triglycerides and are reacted in a second step with electrolytically generated protons to give glycerol and the respective alkali metal hydroxide.

[0008] The prior art accordingly describes processes that are performed in electrolysis cells with an ion-permeable layer, for example NaSICON solid-state electrolytes. However, these solid-state electrolytes typically have the disadvantage that they lack long-term stability towards aqueous acids. This is problematic in that, during the electrolysis in the anode chamber, the pH falls as a result of oxidation processes (for example in the case of production of halogens by disproportionation or by oxygen formation). These acidic conditions attack the NaSICON solid-state electrolyte to such a degree that the process cannot be used on an industrial scale. In order to counter this problem, various approaches have been described in the prior art.

[0009] For instance, three-chamber cells have been proposed in the prior art. These are known in the field of electrodialysis, for example U.S. Pat. No. 6,221,225 B1.

[0010] WO 2012/048032 A2 and US 2010/0044242 A1 describe, for example, electrochemical processes for preparing sodium hypochlorite and similar chlorine compounds in such a three-chamber cell. The cathode chamber and the middle chamber of the cell are separated here by a solid-state electrolyte permeable to cations, for example NaSICON. In order to protect this from the acidic anolyte, the middle chamber is supplied, for example, with solution from the cathode chamber. US 2010/0044242 A1 also describes, in FIG. 6, the possibility of mixing solution from the middle chamber with solution from the anode chamber outside the chamber in order to obtain sodium hypochlorite.

[0011] Such cells have also been proposed in the prior art for the production or purification of alkali metal alkoxides.

[0012] For instance, U.S. Pat. No. 5,389,211 A describes a process for purifying alkoxide solutions in which a three-chamber cell is used, in which the chambers are delimited from one another by cation-selective solid-state electrolytes or else nonionic dividing walls. The middle chamber is used as buffer chamber in order to prevent the purified alkoxide or hydroxide solution from the cathode chamber from mixing with the contaminated solution from the anode chamber.

[0013] DE 42 33 191 A1 describes the electrolytic recovery of alkoxides from salts and alkoxides in multichamber cells and stacks of multiple cells.

[0014] WO 2008/076327 A1 describes a process for producing alkali metal alkoxides. This uses a three-chamber cell, the middle chamber of which has been filled with alkali metal alkoxide (see, for example, paragraphs and of WO 2008/076327 A1). This protects the solid-state electrolyte separating the middle chamber and the cathode chamber from the solution present in the anode chamber, which becomes more acidic in the course of electrolysis. A similar arrangement is described by WO 2009/073062 A1. However, this arrangement has the disadvantage that the alkali metal alkoxide solution is the desired product, but this is consumed and continuously contaminated as buffer solution. A further disadvantage of the process described in WO 2008/076327 A1 is that the formation of the alkoxide in the cathode chamber depends on the diffusion rate of the alkali metal ions through two membranes or solid-state electrolytes. This in turn leads to slowing of the formation of the alkoxide.

[0015] A further problem results from the geometry of the three-chamber cell. The middle chamber in such a chamber

is separated from the anode chamber by a diffusion barrier and from the cathode chamber by an ion-conducting ceramic. During the electrolysis, this results unavoidably in development of pH gradients and in dead volumes. This can damage the ion-conducting ceramic and, as a result, increase the voltage demand of the electrolysis and/or lead to fracture of the ceramic.

[0016] While this effect takes place throughout the electrolysis chamber, the drop in pH is particularly critical in the middle chamber since this is bounded by the ion-conducting ceramic. Gases are typically formed at the anode and the cathode, such that there is at least some degree of mixing in these chambers. By contrast, no such mixing takes place in the middle chamber, such that the pH gradient develops therein. This unwanted effect is enhanced by the fact that the brine is generally pumped relatively slowly through the electrolysis cell.

[0017] It was therefore an object of the present invention to provide an improved process for electrolytic production of alkali metal alkoxides, and also an electrolysis chamber especially suitable for such a process. These are not to have the aforementioned disadvantages, and are especially to assure improved protection of the solid-state electrolyte prior to the formation of the pH gradient and more sparing use of the reactants compared to the prior art.

2. BRIEF DESCRIPTION OF THE INVENTION

[0018] What have now been found, surprisingly, are an electrolysis cell and a process that solve the problem addressed by the invention.

[0019] The electrolysis cell E <100> in the first aspect of the invention comprises at least one anode chamber K_A <101>, at least one cathode chamber K_K <102> and at least one interposed middle chamber K_M <103>.

[0020] wherein K_A <101> comprises an anodic electrode E_A <104> and an outlet A_{KA} <106>.

[0021] wherein K_K <102> comprises a cathodic electrode E_K <105>, an inlet Z_{KK} <107> and an outlet A_{KK} <109>.

[0022] wherein K_M <103> comprises an inlet Z_{KM} <108>, is divided from K_A <101> by a diffusion barrier D <110> and is divided from K_K <102> by an alkali metal cation-conducting solid-state electrolyte F_K <111>.

[0023] wherein K_M <103> and K_A <101> are connected to one another by a connection V_{AM} <112> through which liquid can be routed from K_M <103> into K_A <101>.

[0024] and is characterized in that the middle chamber K_M <103> comprises internals <120>.

[0025] wherein the internals <120> are configured to lead to turbulence and vortexing in an electrolyte L_3 <114> that flows through the middle chamber K_M <103>.

[0026] In a second aspect, the present invention relates to a process for producing a solution L_1 <115> of an alkali metal alkoxide XOR in the alcohol ROH in an electrolysis cell E <100> according to the first aspect of the invention.

[0027] wherein the process comprises the following steps (a), (b) and (c) that proceed simultaneously:

[0028] (a) a solution L_2 <113> comprising the alcohol ROH is routed through K_K <102>.

[0029] (b) a neutral or alkaline, aqueous solution L_3 <114> of a salt S comprising X as cation is routed through K_M , then via V_{AM} , then through K_A <101>.

[0030] (c) voltage is applied between E_A <104> and E_K <105>.

[0031] which affords the solution L_1 <115> at the outlet A_{KK} <109>, with a higher concentration of XOR in L_1 <115> than in L_2 <113>.

[0032] and which affords an aqueous solution L_4 <116> of S at the outlet A_{KA} <106>, with a lower concentration of S in L_4 <116> than in L_3 <114>.

[0033] wherein X is an alkali metal cation and R is an alkyl radical having 1 to 4 carbon atoms.

3. FIGURES

[0034] FIG. 1 shows a preferred embodiment of an electrolysis cell <100> according to the invention and of the process according to the invention. The three-chamber cell E <100> comprises a cathode chamber K_K <102>, an anode chamber K_A <101> and an interposed middle chamber K_M <103>.

[0035] The cathode chamber K_K <102> comprises a cathodic electrode E_K <105>, an inlet Z_{KK} <107> and an outlet A_{KK} <109>.

[0036] The anode chamber K_A <101> comprises an anodic electrode E_A <104> and an outlet A_{KA} <106> and is connected to the middle chamber K_M <103> via the connection V_{AM} <112>.

[0037] The middle chamber K_M <103> comprises an inlet Z_{KM} <108>.

[0038] The three chambers are bounded by an outer wall <117> of the three-chamber cell E <100>. The cathode chamber K_K <102> is also separated from the middle chamber K_M <103> by an NaSICON solid-state electrolyte F_K <111> which is selectively permeable to sodium ions. The middle chamber K_M <103> is additionally separated in turn from the anode chamber K_A <101> by a diffusion barrier D <110>. The NaSICON solid-state electrolyte F_K <111> and the diffusion barrier D <110> extend over the entire depth and height of the three-chamber cell E <100>. The diffusion barrier D <110> is made of glass.

[0039] In the embodiment according to FIG. 1, the connection V_{AM} <112> is formed outside the electrolysis cell E <100>, especially by a tube or hose, the material of which may be selected from rubber, metal and plastic. Through the connection V_{AM} <112>, it is possible to route liquid from the middle chamber K_M <103> into the anode chamber K_A <101> outside the outer wall W_A <117> of the three-chamber cell E <100>. The connection V_{AM} <112> connects an outlet A_{KM} <118> that penetrates the outer wall W_A <117> of the electrolysis cell E <100> at the base of the middle chamber K_M <103> to an inlet Z_{KA} <119> that penetrates the outer wall W_A <117> of the electrolysis cell E <100> at the base of the anode chamber K_A <101>.

[0040] An aqueous solution of sodium chloride L_3 <114> with pH 10.5 is introduced via the inlet Z_{KM} <108>, in the direction of gravity, into the middle chamber K_M <103>. The connection V_{AM} <112> formed between an outlet A_{KM} <118> from the middle chamber K_M <103> and an inlet Z_{KA} <119> to the anode chamber K_A <101> connects the middle chamber K_M <103> to the anode chamber K_A <101>. Sodium chloride solution L_3 <114> is routed through this connection V_{AM} <112> from the middle chamber K_M <103> into the anode chamber K_A <101>.

[0041] A solution of sodium methoxide in methanol L_2 <113> is routed into the cathode chamber K_K <102> via the inlet Z_{KK} <107>.

[0042] At the same time, a voltage is applied between the cathodic electrode E_K <105> and the anodic electrode E_A <104>. This results in reduction of methanol in the electrolyte L_2 <113> to give methoxide and H_2 in the cathode chamber K_K <102> ($CH_3OH + e^- \rightarrow CH_3O^- + \frac{1}{2} H_2$). At the same time, sodium ions diffuse from the middle chamber K_M <103> through the NaSICON solid-state electrolyte F_K <111> into the cathode chamber K_K <102>. Overall, this increases the concentration of sodium methoxide in the cathode chamber K_K <102>, which affords a methanolic solution of sodium methoxide L_1 <115>, the sodium methoxide concentration of which is elevated compared to L_2 <113>.

[0043] In the anode chamber K_A <101>, the oxidation of chloride ions takes place to give molecular chlorine ($Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-$). In the outlet A_{KA} <106>, an aqueous solution L_4 <116> is obtained, in which the content of NaCl is reduced compared to L_3 <114>. Chlorine gas (Cl_2) in water, according to the reaction $Cl_2 + H_2O \rightarrow HOCl + HCl$, forms hypochlorous acid and hydrochloric acid, which give an acidic reaction with further water molecules. The acidity damages the NaSICON solid-state electrolyte <111>, but is restricted to the anode chamber K_A <101> by the arrangement according to the invention, and hence kept away from the NaSICON solid-state electrolyte F_K <111> in the electrolysis cell E <100>. This considerably increases the lifetime thereof.

[0044] In the middle chamber K_M <103>, there are also internals <120> in the form of a mesh-like wire basket <122> which contains glass or plastic beads <121>. The wire basket <122> is placed loosely in the middle chamber K_M <103>, but may also be secured on the inside of the outer wall of <117>. The aqueous solution L_3 <114> supplied through the inlet Z_{KM} <108> is guided through these internals <120>, which results in vortexing and turbulence. This turbulence L_3 <114> in the solution prevents buildup of a pH gradient in the middle chamber K_M <103> with progressive electrolysis, and thus prevents the development of a low pH in the solution directly adjoining the NaSICON solid-state electrolyte <111>. This further increases the service life of the NaSICON solid-state electrolyte <111>.

[0045] FIG. 2 shows a further embodiment of the electrolysis cell according to the invention and the process according to the invention corresponding to that shown in FIG. 1. One difference here is that the connection V_{AM} <112> from the middle chamber K_M <103> to the anode chamber K_A <101> is formed by a perforation in the diffusion barrier D <110>. Also provided as internals <120>, rather than the wire basket <122> present loose in the middle chamber K_M <103>, are multiple glass or plastic studs <123-2> that project into the middle chamber K_M <103> on the NaSICON solid-state electrolyte F_K <111>. Alternatively or additionally, it is also possible to provide corresponding studs <123-1> on the diffusion barrier D <110>. As in the embodiment shown in FIG. 1 too, the aqueous solution L_3 <114> supplied through the inlet Z_{KM} <108> is vortexed by these internals <120>. This turbulence in the solution L_3 <114> destroys the pH gradient that builds up in the middle chamber K_M <103> with progressive electrolysis.

4. DETAILED DESCRIPTION OF THE INVENTION

4.1 Electrolysis Cell E

[0046] The first aspect of the invention relates to an electrolysis cell E <100>. The electrolysis cell E <100> in the first aspect of the invention comprises at least one anode chamber K_A <101>, at least one cathode chamber K_K <102> and at least one interposed middle chamber K_M <103>. This also includes electrolysis cells E <100> having more than one anode chamber K_A <101> and/or cathode chamber K_K <102> and/or middle chamber K_M <103>. Such electrolysis cells in which these chambers are joined to one another in the form of modules are described, for example, in DD 258 143 A3 and US 2006/0226022 A1.

[0047] The anode chamber K_A <101> comprises an anodic electrode E_A <104>. A useful anodic electrode E_A <104> of this kind is any electrode familiar to the person skilled in the art that is stable under the conditions of the process according to the invention in the second aspect of the invention. These are described, in particular, in WO 2014/008410 A1, paragraph or DE 10360758 A1, paragraph [031]. This electrode E_A <104> may consist of one layer or consist of multiple planar layers parallel to one another that may each be perforated or expanded. The anodic electrode E_A <104> especially comprises a material selected from the group consisting of ruthenium oxide, iridium oxide, nickel, cobalt, nickel tungstate, nickel titanate, precious metals such as, in particular, platinum, supported on a support such as titanium or Kovar® (an iron/nickel/cobalt alloy in which the individual components are preferably as follows: 54% by mass of iron, 29% by mass of nickel, 17% by mass of cobalt). Further possible anode materials are especially stainless steel, lead, graphite, tungsten carbide, titanium diboride. Preferably, the anodic electrode E_A <104> comprises a titanium anode coated with ruthenium oxide/iridium oxide ($RuO_2 + IrO_2/Ti$).

[0048] The cathode chamber K_K <102> comprises a cathodic electrode E_K <105>. A useful cathodic electrode E_K <105> of this kind is any electrode familiar to the person skilled in the art that is stable under the conditions. These are described, in particular, in WO 2014/008410 A1, paragraph or DE 10360758 A1, paragraph [030]. This electrode E_K <105> may be selected from the group consisting of mesh wool, three-dimensional matrix structure and "balls". The cathodic electrode E_K <105> especially comprises a material selected from the group consisting of steel, nickel, copper, platinum, platinized metals, palladium, carbon-supported palladium, titanium. Preferably, E_K <105> comprises nickel.

[0049] The at least one middle chamber K_M <103> is between the anode chamber K_A <101> and the cathode chamber K_K <102>.

[0050] The electrolysis cell E <100> typically has an outer wall W_A <117>. The outer wall W_A <117> is especially made from a material selected from the group consisting of steel, preferably rubberized steel, plastic, especially from Telene® (thermoset polydicyclopentadiene), PVC (polyvinylchloride), PVC-C (post-chlorinated polyvinylchloride), PVDF (polyvinylidene fluoride). W_A <117> may especially be perforated for inlets and outlets. Within W_A <117> are then the at least one anode chamber K_A <101>, the at least one cathode chamber K_K <102> and the at least one interposed middle chamber K_M <103>.

[0051] $K_M <103>$ is separated from $K_A <101>$ by a diffusion barrier $D <110>$ and from $K_K <102>$ by an alkali metal cation-conducting solid-state electrolyte $F_K <111>$.

[0052] For the diffusion barrier $D <110>$, it is possible to use any material that is stable under the conditions of the process according to the invention in the second aspect of the invention and prevents or slows the transfer of protons from the liquid present in the anode chamber $K_A <101>$ into the middle chamber $K_M <103>$.

[0053] The diffusion barrier $D <110>$ used is especially a non-ion-specific dividing wall or a membrane permeable to specific ions. The diffusion barrier $D <110>$ is preferably a non-ion-specific dividing wall.

[0054] The material of the non-ion-specific dividing wall is especially selected from the group consisting of fabric, which is especially textile fabric or metal weave, glass, which is especially sintered glass or glass frits, ceramic, especially ceramic frits, membrane diaphragms, and is more preferably glass.

[0055] If the diffusion barrier $D <110>$ is a “membrane permeable to specific ions”, what this means in accordance with the invention is that the respective membrane promotes the diffusion of particular ions therethrough over other ions. More particularly, what this means is membranes that promote the diffusion therethrough of ions of a particular charge type over ions of the opposite charge. Even more preferably, membranes permeable to specific ions also promote the diffusion of particular ions of one charge type over other ions of the same charge type therethrough.

[0056] If the diffusion barrier $D <110>$ is a “membrane permeable to specific ions”, the diffusion barrier $D <110>$ is especially an anion-conducting membrane or a cation-conducting membrane.

[0057] According to the invention, anion-conducting membranes are those that selectively conduct anions, preferably selectively conduct particular anions. In other words, they promote the diffusion of anions therethrough over that of cations, especially over protons; even more preferably, they additionally promote the diffusion of particular anions therethrough over the diffusion of other anions therethrough.

[0058] According to the invention, cation-conducting membranes are those that selectively conduct cations, preferably selectively conduct particular cations. In other words, they promote the diffusion of cations therethrough over that of anions; even more preferably, they additionally promote the diffusion of particular cations therethrough over the diffusion of other cations therethrough, more preferably still that of cations that are not protons, more preferably sodium cations, over protons.

[0059] What is meant more particularly by “promote the diffusion of particular ions X over the diffusion of other ions Y” is that the coefficient of diffusion (unit: m^2/s) of ion type X at a given temperature for the membrane in question is higher by a factor of 10, preferably 100, preferably 1000, than the coefficient of diffusion of ion type Y for the membrane in question.

[0060] If the diffusion barrier $D <110>$ is a “membrane permeable to specific ions”, it is preferably an anion-conducting membrane since this particularly efficiently prevents the diffusion of protons from the anode chamber $K_A <101>$ into the middle chamber $K_M <103>$.

[0061] The anion-conducting membrane used is especially one selective for the anions encompassed by the salt S. Such membranes are known to and can be used by the person skilled in the art.

[0062] The salt S is preferably a halide, sulfate, sulfite, nitrate, hydrogencarbonate or carbonate of X, even more preferably a halide.

[0063] Halides are fluorides, chlorides, bromides, iodides. The most preferred halide is chloride.

[0064] The anion-conducting membrane used is preferably one selective for halides, preferably chloride.

[0065] Anion-conducting membranes are described, for example, by M. A. Hickner, A. M. Herring, E. B. Coughlin, *Journal of Polymer Science, Part B: Polymer Physics* 2013, 51, 1727-1735, by C. G. Arges, V. Ramani, P. N. Pintauro, *Electrochemical Society Interface* 2010, 19, 31-35, in WO 2007/048712 A2, and on page 181 of the textbook by Volkmar M. Schmidt, *Elektrochemische Verfahrenstechnik: Grundlagen, Reaktionstechnik, Prozessoptimierung* [Electrochemical Engineering: Fundamentals, Reaction Technology, Process Optimization], 1st edition (8 Oct. 2003).

[0066] Even more preferably, anion-conducting membranes used are accordingly organic polymers that are especially selected from polyethylene, polybenzimidazoles, polyether ketones, polystyrene, polypropylene and fluorinated membranes such as polyperfluoroethylene, preferably polystyrene, where these have covalently bonded functional groups selected from $-\text{NH}_3^+$, $-\text{NRH}_2^+$, $-\text{NR}_3^+$, $=\text{NR}^+$, $-\text{PR}_3^+$, where R is alkyl groups having preferably 1 to 20 carbon atoms, or other cationic groups. They preferably have covalently bonded functional groups selected from $-\text{NH}_3^+$, $-\text{NRH}_2^+$ and $-\text{NR}_3^+$, more preferably selected from $-\text{NH}_3^+$ and $-\text{NR}_3^+$, even more preferably $-\text{NR}_3^+$.

[0067] If the diffusion barrier $D <110>$ is a cation-conducting membrane, it is especially a membrane selective for the cations encompassed by the salt S. Even more preferably, the diffusion barrier $D <110>$ is an alkali metal cation-conducting membrane, even more preferably a potassium and/or sodium ion-conducting membrane, most preferably a sodium ion-conducting membrane.

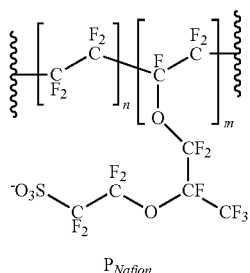
[0068] Cation-conducting membranes are described, for example, on page 181 of the textbook by Volkmar M. Schmidt, *Elektrochemische Verfahrenstechnik: Grundlagen, Reaktionstechnik, Prozessoptimierung*, 1st edition (8 Oct. 2003).

[0069] Even more preferably, cation-conducting membranes used are accordingly organic polymers that are especially selected from polyethylene, polybenzimidazoles, polyether ketones, polystyrene, polypropylene and fluorinated membranes such as polyperfluoroethylene, preferably polystyrene and polyperfluoroethylene, where these bear covalently bonded functional groups selected from SO_3^- , $-\text{COO}^-$, $-\text{PO}_3^{2-}$ and $-\text{PO}_2\text{H}^-$, preferably $-\text{SO}_3^-$ (described in DE 10 2010 062 804 A1, U.S. Pat. No. 4,831,146).

[0070] This may be, for example, a sulfonated polyperfluoroethylene (Nafion® with CAS number: 31175-20-9). These are known to the person skilled in the art, for example from WO 2008/076327 A1, paragraph [058], US 2010/0044242 A1, paragraph or US 2016/0204459 A1, and are commercially available under the Nation®, Aciplex® F, Flemion®, Neosepta®, Ultrex®, PC-SK® trade names. Neosepta® membranes are described, for example, by S. A.

Mareev, D. Yu. Butylskii, N. D. Pismenskaya, C. Larchet, L. Dammak, V. V. Nikonenko, *Journal of Membrane Science* 2018, 563, 768-776.

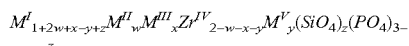
[0071] If a cation-conducting membrane is used as diffusion barrier D <110>, this may, for example, be a polymer functionalized with sulfonic acid groups, especially of the formula P_{NAFION} below, where n and m may independently be a whole number from 1 to 10^6 , preferably a whole number from 10 to 10^5 , more preferably a whole number from 10^2 to 10^4 .



[0072] A useful alkali metal cation-conducting solid-state electrolyte F_K <111> is any solid-state electrolyte that can transport cations, especially alkali metal cations, even more preferably sodium cations, from the middle chamber K_M <103> into the cathode chamber K_K <102>. Such solid-state electrolytes are known to the person skilled in the art and are described, for example, in DE 10 2015 013 155 A1, in WO 2012/048032 A2, paragraphs [0035], [0039], [0040], in US 2010/0044242 A1, paragraphs [0040], [0041], in DE 10360758 A1, paragraphs to [025]. They are sold commercially under the NaSICON, LISICON, KSICON name. A sodium ion-conducting solid-state electrolyte F_K <111> is preferred, and this even more preferably has a NaSICON structure. NaSICON structures usable in accordance with the invention are also described, for example, by N. Anantharamulu, K. Koteswara Rao, G. Rambabu, B. Vijaya Kumar, Velchuri Radha, M. Vithal, *J Mater Sci* 2011, 46, 2821-2837.

NaSICON Preferably has a Structure of the Formula

[0073]



[0074] M^I is selected from Na^+ , Li^+ , preferably Na^+ .

[0075] M^{II} is a divalent metal cation, preferably selected from Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Co^{2+} , Ni^{2+} , more preferably selected from Co^{2+} , Ni^{2+} .

[0076] M^{III} is a trivalent metal cation, preferably selected from Al^{3+} , Ga^{3+} , Sc^{3+} , La^{3+} , Y^{3+} , Gd^{3+} , Sm^{3+} , Lu^{3+} , Fe^{3+} , Cr^{3+} , more preferably selected from Sc^{3+} , La^{3+} , Y^{3+} , Gd^{3+} , Sm^{3+} , especially preferably selected from Sc^{3+} , Y^{3+} , La^{3+} .

[0077] M^V is a pentavalent metal cation, preferably selected from V^{5+} , Nb^{5+} , Ta^{5+} .

[0078] The Roman indices I, II, III, IV, V indicate the oxidation numbers in which the respective metal cations exist.

[0079] w, x, y, z are real numbers, where $0 \leq x < 2$, $0 \leq y < 2$, $0 \leq w < 2$, $0 \leq z < 3$, and where w, x, y, z are chosen such that $1+2w+x-y+z \geq 0$ and $2-w-x-y \geq 0$.

[0080] Even more preferably in accordance with the invention, NaSICON has a structure of the formula $Na_{(1+v)}Zr_2Si_vP_{(3-v)}O_{12}$ where v is a real number for which $0 \leq v \leq 3$. Most preferably, $V=2.4$.

[0081] The cathode chamber K_K <102> also comprises an inlet Z_{KK} <107> and an outlet A_{KK} <109> that enables addition of liquid, for example the solution L_2 <113>, to the cathode chamber K_K <102> and removal of liquid present therein, for example the solution L_1 <115>. The inlet Z_{KK} <107> and the outlet A_{KK} <109> are mounted on the cathode chamber K_K <102> in such a way that the solution comes into contact with the cathodic electrode E_K <105> as it flows through the cathode chamber K_K <102>. This is a prerequisite for the solution L_1 <115> to be obtained at the outlet A_{KK} <109> in the performance of the process according to the invention in the second aspect of the invention when the solution L_2 <113> of an alkali metal alkoxide XOR in the alcohol ROH is routed through K_K <102>.

[0082] The anode chamber K_A <101> also comprises an outlet A_{KA} <106> that enables removal of liquid present in the anode chamber K_A <101>, for example the aqueous solution L_4 <106>. In addition, the middle chamber K_M <103> comprises an inlet Z_{KM} <108>, while K_A <101> and K_M <103> are connected to one another by a connection V_{AM} <112> through which liquid can be routed from K_M <103> into K_A <101>. As a result, a solution L_3 <114> can be introduced via the inlet Z_{KM} <108> to K_M <103>, and this can be routed through K_M <103>, then via V_{AM} <112>, into the anode chamber K_A <101>, and finally through the anode chamber K_A <101>. V_{AM} <112> and the outlet A_{KA} <106> are mounted on the anode chamber K_A <101> in such a way that the solution L_3 <114> comes into contact with the anodic electrode E_A <104> as it flows through the anode chamber K_A <101>. This is a prerequisite for the aqueous solution L_4 <116> to be obtained at the outlet A_{KA} <106> in the performance of the process according to the invention in the second aspect when the solution L_3 <114> is routed first through K_M <103>, then V_{AM} <112>, then K_A <101>.

[0083] The inlets Z_{KK} <107>, Z_{KM} <108>, Z_{KA} <119> and outlets A_{KK} <109>, A_{KA} <106>, A_{KM} <118> may be mounted on the electrolysis cell E <100> by methods known to the person skilled in the art.

[0084] The connection V_{AM} <112> may be formed within the electrolysis cell E <100> and/or outside, preferably within, the electrolysis cell E <100>.

[0085] If the connection V_{AM} <112> is formed within the electrolysis cell E <100>, it is preferably formed by at least one perforation in the diffusion barrier D <110>.

[0086] If the connection V_{AM} <112> is formed outside the electrolysis cell E <100>, it is preferably formed by a connection of K_M <103> and K_A <101> that runs outside the electrolysis cell E <100>, especially in that an outlet A_{KM} <118> through the outer wall W_A <117> is formed in the middle chamber K_M <103>, preferably at the base of the middle chamber K_M <103>, the inlet Z_{KM} <108> more preferably being at the top end of the middle chamber K_M <103>, and an inlet Z_{KA} <119> through the outer wall W_A <117> is formed in the anode chamber K_A <101>, preferably at the base of the anode chamber K_A <101>, and these are connected by a conduit, for example a pipe or a hose, preferably comprising a material selected from rubber and plastic. The outlet A_{KA} <106> is then more preferably at the top end of the anode chamber K_A <101>.

[0087] What is meant by “outlet A_{KM} <118> at the base of the middle chamber K_M <103>” is that the outlet A_{KM} <118> is attached to the electrolysis cell E <100> in such a way that the solution L_4 <114> leaves the middle chamber K_M <103> in the direction of gravity.

[0088] What is meant by “inlet Z_{KA} <119> at the base of the anode chamber K_A <101>” is that the inlet Z_{KA} <119> is attached to the electrolysis cell E <100> in such a way that the solution L_3 <114> enters the anode chamber K_A <101> counter to gravity.

[0089] What is meant by “inlet Z_{KM} <108> at the top end of the middle chamber K_M <103>” is that the inlet Z_{KM} <108> is attached to the electrolysis cell E <100> in such a way that the solution L_3 <114> enters the middle chamber K_M <103> in the direction of gravity.

[0090] What is meant by “outlet A_{KA} <106> at the top end of the anode chamber K_A <101>” is that the outlet A_{KA} <106> is mounted on the electrolysis cell E <100> in such a way that the solution L_4 <116> leaves the anode chamber K_A <101> counter to gravity.

[0091] This embodiment is particularly advantageous and therefore preferred when the outlet A_{KM} <118> is formed by the outer wall W_A <117> at the base of the middle chamber K_M <103>, and the inlet Z_{KA} <119> by the outer wall W_A <117> at the base of the anode chamber K_A <101>. This arrangement makes it possible in a particularly simple manner to remove gases formed in the anode chamber K_A from the anode chamber K_A <101> with L_4 <116>, in order to separate them further.

[0092] When the connection V_{AM} <112> is formed outside the electrolysis cell E <100>, in particular, Z_{KM} <108> and A_{KM} <118> are arranged at opposite ends of the outer wall W_A <117> of the middle chamber K_M <103> (i.e. Z_{KM} <108> at the base and A_{KM} <118> at the top end of the electrolysis cell E <100> or vice versa) and Z_{KA} <119> and A_{KA} <106> are arranged at opposite ends of the outer wall W_A <117> of the anode chamber K_A <101> (i.e. Z_{KA} <119> at the base and A_{KA} <106> at the top end of the electrolysis cell E <100> or vice versa), as shown more particularly in FIG. 1. By virtue of this geometry, L_3 <114> must flow through the two chambers K_M <103> and K_A <101>. It is possible here for Z_{KA} <119> and Z_{KM} <108> to be formed on the same side of the electrolysis cell E <100>, in which case A_{KM} <118> and A_{KA} <106> are automatically also formed on the same side of the electrolysis cell E <100>. Alternatively, as shown in FIG. 1, it is possible for Z_{KA} <119> and Z_{KM} <108> to be formed on opposite sides of the electrolysis cell E <100>, in which case A_{KM} <118> and A_{KA} <106> are automatically also formed on opposite sides of the electrolysis cell E <100>.

[0093] When the connection V_{AM} <112> is formed within the electrolysis cell E <100>, this may especially be implemented in that one side (“side A”) of the electrolysis cell E <100>, which is the top end or the base of the electrolysis cell E <100>, preferably the top end as shown in FIG. 2, comprises the inlet Z_{KM} <108> and the outlet A_{KA} <106>, and the diffusion barrier D <110> extends proceeding from this side (“side A”) into the electrolysis cell E <100>, but does not quite reach up to the side (“side B”) of the electrolysis cell E <100> opposite side A, which is then the base or the top end of the electrolysis cell E <100>, and at the same time covers 50% or more of the height of the three-chamber cell E <100>, preferably 60% to 99% of the height of the three-chamber cell E <100>, more preferably

70% to 95% of the height of the three-chamber cell E <100>, even more preferably 80% to 90% of the height of the three-chamber cell E <100>, more preferably still 85% of the height of the three-chamber cell E <100>. Because the diffusion barrier D <110> does not touch side B of the three-chamber cell E <100>, a gap thus arises between diffusion barrier D <110> and the outer wall W_A <117> of side B of the three-chamber cell E <100>. In that case, the gap is the connection V_{AM} <112>. By virtue of this geometry, L_3 <114> must flow completely through the two chambers K_M <103> and K_A <101>.

[0094] These embodiments best assure that the aqueous salt solution L_3 <114> flows past the acid-sensitive solid-state electrolyte before it comes into contact with the anodic electrode E_A <104>, which results in the formation of acids.

[0095] According to the invention, “base of the electrolysis cell E <100>” is the side of the electrolysis cell E <100> through which a solution (e.g. L_3 <114> in the case of A_{KM} <118> in FIG. 1) exits from the electrolysis cell E in the same direction as gravity, or the side of the electrolysis cell E through which a solution (e.g. L_2 <113> in the case of Z_{KK} <107> in FIGS. 1 and 2, and L_3 <114> in the case of A_{KA} <119> in FIG. 1) is supplied to the electrolysis cell E counter to gravity.

[0096] According to the invention, “top end of the electrolysis cell E” is the side of the electrolysis cell E through which a solution (e.g. L_4 <116> in the case of A_{KA} <106> and L_1 <115> in the case of A_{KK} <109> in FIGS. 1 and 2) exits from the electrolysis cell E counter to gravity, or the side of the electrolysis cell E through which a solution (e.g. L_3 <114> in the case of Z_{KM} <108> in FIGS. 1 and 2) is supplied to the electrolysis cell E in the same direction as gravity.

[0097] According to the invention, the middle chamber K_M comprises internals <120>. According to the invention, internals <120> are in the solid state of matter. Suitable internals of this kind are any articles or structures known to the person skilled in the art that are sufficiently inert to the electrolysis conditions.

[0098] The internals <120> especially comprise at least one material selected from rubber; plastic, which is especially selected from polystyrene, polypropylene, PVC, PVC-C; glass; porcelain; metal. The metal is especially a metal or an alloy of two or more metals selected from titanium, iron, molybdenum, chromium, nickel, preferably an alloy comprising at least two metals selected from titanium, iron, molybdenum, chromium, nickel, even more preferably a steel alloy comprising, as well as iron, at least one further metal selected from titanium, molybdenum, chromium, nickel, and is most preferably stainless steel.

[0099] The internals <120> are especially selected from structured packings, unstructured packings (random packings) and trays, e.g. bubble-cap trays, valve trays, tunnel-cap trays, Thormann trays, cross-slot bubble cap trays or sieve trays.

[0100] Unstructured packings are generally random packings. Random packings used are typically Raschig rings, Pall rings, Berl saddles or Intalox® saddles. Structured packings are sold, for example, under the Mellapak® trade name by Sulzer.

[0101] The internals <120> may be loose in the middle chamber K_M <103>, for example spheres <121>, for instance made of glass, in a basket composed of wire framework <122>, as shown in FIG. 1.

[0102] Alternatively, the internals <120> may also be secured, for example on the solid-state electrolyte F_K <111>, on the diffusion barrier D <110>, or on the outer wall <117> that bounds the inside of the middle chamber K_M <103>. The securing can be effected by methods known to the person skilled in the art, for example by screw connection, clamping, adhesive bonding (polymer adhesive, PVC adhesive).

[0103] Accordingly, the studs <123-2> shown in FIG. 2 are mounted on the solid-state electrolyte F_K <111>, and the studs <123-1> on the diffusion barrier D <110>. Corresponding studs may also be mounted on the outer wall <117> that bounds the inside of the middle chamber K_M <103>, and in that case form stalactite- or stalagmite-like structures in the middle chamber.

[0104] Securing of the internals <120> on the alkali metal cation-conducting solid-state electrolyte F_K <111> or on the diffusion barrier D <110> can be accomplished, for example, by securing them to a wire frame on the wall in question.

[0105] In a preferred embodiment of the electrolysis cell E <100> according to the first aspect of the invention, the internals <120> account for a proportion ζ of 1% to 99%, more preferably 10% to 99%, even more preferably 40% to 90%, even more preferably 50% to 90%, even more preferably 60% to 90%, most preferably 80% to 90%, of the volume encompassed by the middle chamber K_M .

[0106] The proportion ζ (in %) is calculated by $\zeta = [(V_O - V_M)/V_O] \cdot 100$.

[0107] V_O here is the maximum volume of liquid, for example the electrolyte L_3 <114>, that can be accommodated by the middle chamber K_M <103> if it does not comprise internals <120>. V_M here is the maximum volume of liquid, for example the electrolyte L_3 <114>, that can be accommodated by the middle chamber K_M <103> if it comprises internals <120>.

[0108] It has been found that, surprisingly, the internals <120> in the middle chamber K_M <103> lead to turbulence and vortexing in the electrolyte L_3 <114> that flows through the middle chamber K_M <103> during the process according to the invention. This slows or entirely prevents the buildup of a pH gradient during the electrolysis, which protects the acid-sensitive solid-state electrolyte F_K <111> and hence enables a longer run time for the electrolysis or extends the lifetime of the electrolysis cell.

[0109] It will be apparent that the internals <120> are mounted in the middle chamber K_M <103> such that they sufficiently enable, or do not completely block, the flow of the electrolyte L_3 <114> through the middle chamber K_M <103> and the anode chamber K_A <101>.

[0110] In a preferred embodiment of the electrolysis cell according to the invention, the internals <120> interrupt the direct pathway in the middle chamber K_M between inlet Z_{KM} <108> and connection V_{AM} <112>.

[0111] Whether the direct route between inlet Z_{KM} <108> and connection V_{AM} <112> in the middle chamber K_M is interrupted is ascertained by the following "thread test":

[0112] 1. A thread is run through the opening through which the inlet Z_{KM} <108> opens into the middle chamber K_M and out of the opening through which the connection V_{AM} <112> opens into the middle chamber K_M . The thread here is sufficiently long that its ends lie outside the middle chamber K_M .

[0113] 2. A force is exerted on the respective ends of the thread in opposing directions, such that the thread becomes taut without breaking.

[0114] 3. If there is at least one thread that is touched by the internals if it is introduced into the middle chamber and tautened in accordance with steps 1. and 2, the feature that the direct route between inlet Z_{KM} <108> and connection V_{AM} <112> in the middle chamber K_M is interrupted is satisfied.

[0115] 4. If there is no thread which, when introduced into the middle chamber and tautened according to steps 1. and 2, is touched by the internals, the feature that the direct route between inlet Z_{KM} <108> and connection V_{AM} <112> in the middle chamber K_M is interrupted is not satisfied.

[0116] The thread is especially made of sewing thread (for example from Gutermann), fishing line, string.

[0117] Most preferably, a fishing line with a diameter of 0.2 mm is used for the thread test, as sold, for example, by Hemingway or Nexos.

4.2 Process According to the Invention

[0118] The process according to the second aspect of the invention is one for producing a solution L_1 <115> of an alkali metal alkoxide XOR in the alcohol ROH in an electrolysis cell E <100> according to the first aspect of the invention.

[0119] The process according to the second aspect of the invention comprises the steps (a), (b) and (c) that proceed simultaneously.

[0120] In step (a), a solution L_2 <113> comprising the alcohol ROH, preferably comprising an alkali metal alkoxide XOR and alcohol ROH, is routed through K_K <102>. X is an alkali metal cation and R is an alkyl radical having 1 to 4 carbon atoms.

[0121] X is preferably selected from the group consisting of Li^+ , K^+ , Na^+ , more preferably from the group consisting of K^+ , Na^+ . Most preferably, $X=Na^+$.

[0122] R is preferably selected from the group consisting of n-propyl, iso-propyl, ethyl and methyl, more preferably from the group consisting of ethyl and methyl. R is most preferably methyl.

[0123] Solution L_2 <113> is preferably free of water. What is meant in accordance with the invention by "free of water" is that the weight of water in solution L_2 <113> based on the weight of the alcohol ROH in solution L_2 <113> (mass ratio) is $\leq 1:10$, more preferably $\leq 1:20$, even more preferably $\leq 1:100$, even more preferably $\leq 0.5:100$.

[0124] If solution L_2 <113> comprises XOR, the proportion by mass of XOR in solution L_2 <113>, based on the overall solution L_2 <113>, is especially >0% to 30% by weight, preferably 5% to 20% by weight, more preferably 10% to 20% by weight, more preferably 10% to 15% by weight, most preferably 13% to 14% by weight, at the very most preferably 13% by weight.

[0125] If solution L_2 <113> comprises XOR, the mass ratio of XOR to alcohol ROH in solution L_2 <113> is especially in the range of 1:100 to 1:5, more preferably in the range of 1:25 to 3:20, even more preferably in the range of 1:12 to 1:8, even more preferably 1:10.

[0126] In step (b), a neutral or alkaline, aqueous solution L_3 <114> of a salt S comprising X as cation is routed through K_M <103>, then via V_{AM} <112>, then through K_A <101>.

[0127] The salt S is preferably a halide, sulfate, sulfite, nitrate, hydrogencarbonate or carbonate of X, even more preferably a halide.

[0128] Halides are fluorides, chlorides, bromides, iodides. The most preferred halide is chloride.

[0129] The pH of the aqueous solution L_3 <114> is ≥ 7.0 , preferably in the range of 7 to 12, more preferably in the range of 8 to 11, even more preferably 10 to 11, most preferably 10.5.

[0130] The proportion by mass of salt S in solution L_3 <113> is preferably in the range of $>0\%$ to 20% by weight, preferably 1% to 20% by weight, more preferably 5% to 20% by weight, even more preferably 10% to 20% by weight, most preferably 20% by weight, based on the overall solution L_3 <113>.

[0131] It has been found that, surprisingly, in step (b), the internals <120> in the middle chamber K_M <103> result in turbulence and vortexing in the electrolyte L_3 <114> that flows through the middle chamber K_M <103> during the process according to the invention. This slows or entirely prevents the buildup of a pH gradient during the electrolysis, which protects the acid-sensitive solid-state electrolyte F_K <111> and hence enables a longer service life of the electrolysis or prolongs the lifetime of the electrolysis cell.

[0132] In step (c), a voltage is then applied between E_A <104> and E_K <105>.

[0133] This results in transfer of current from the charge source to the anode, transfer of charge via ions to the cathode and ultimately transfer of current back to the charge source. The charge source is known to the person skilled in the art and is typically a rectifier that converts alternating current to direct current and can generate particular voltages via voltage transformers.

[0134] This in turn has the following consequences:

[0135] solution L_1 <115> is obtained at the outlet A_{KK} <109>, with a higher concentration of XOR in L_1 <115> than in L_2 <113>.

[0136] an aqueous solution L_4 <116> of S is obtained at the outlet A_{KA} <106>, with a lower concentration of S in L_4 <116> than in L_3 <114>.

[0137] In the process according to the second aspect of the invention, in particular, such a voltage is applied that such a current flows that the current density (=ratio of the current supplied to the electrolysis cell to the area of the solid-state electrolyte in contact with the anolyte present in the middle chamber K_M <103>) is in the range from 10 to 8000 A/m², more preferably in the range from 100 to 2000 A/m², even more preferably in the range from 300 to 800 A/m², and even more preferably is 494 A/m². This can be determined in a standard manner by the person skilled in the art. The area of the solid-state electrolyte in contact with the anolyte present in the middle chamber K_M <103> is especially 0.00001 to 10 m², preferably 0.0001 to 2.5 m², more preferably 0.0002 to 0.15 m², even more preferably 2.83 cm².

[0138] It will be apparent that step (c) of the process according to the second aspect of the invention is performed when the two chambers K_M <103> and K_A <101> are at least partly laden with L_3 <114> and K_K <102> is at least partly laden with L_2 <113>.

[0139] The fact that in step (c) transfer of charge takes place between E_A <104> and E_K <105> implies that K_K <102>, K_M <103> and K_A <101> are simultaneously laden

with L_2 <113> or L_3 <114> such that they cover the electrodes E_A <104> and E_K <105> to such an extent that the circuit is complete.

[0140] This is the case especially when a liquid stream of L_3 <114> is routed continuously through K_M <103>, V_{AM} <112> and K_A <101> and a liquid stream of L_2 <113> through K_K <102>, and the liquid stream of L_3 <114> covers electrode E_A <104> and the liquid stream of L_2 <113> covers electrode E_K <105> at least partly, preferably completely.

[0141] Because the stream of the electrolyte L_3 <114> meets the internals in the middle chamber K_M <103>, there is no formation of a typical pH gradient in this chamber. This effect is even stronger when the internals <120> break the direct pathway in the middle chamber K_M between inlet Z_{KM} <108> and connection V_{AM} <112>, since these internals <120> are then within the flow pathway of the electrolyte L_3 <114> through the middle chamber K_M <103> and disrupt unhindered flow.

[0142] This desired effect is preferably amplified in the process according to the second aspect of the invention by varying the flow rate of the electrolyte L_3 <114> through the middle chamber K_M <103> during the performance of step (b), which can produce further turbulence that disrupts the formation of a pH gradient.

[0143] In a further preferred embodiment, the process according to the second aspect of the invention is performed continuously, i.e. step (a) and step (b) are performed continuously, while applying voltage as per step (c).

[0144] After performance of step (c), solution L_1 <115> is obtained at the outlet A_{KK} <109>, with the concentration of XOR in L_1 <115> being higher than in L_2 <113>. If L_2 <113> already comprised XOR, the concentration of XOR in L_1 <115> is preferably 1.01 to 2.2 times, more preferably 1.04 to 1.8 times, even more preferably 1.077 to 1.4 times, even more preferably 1.077 to 1.08 times, higher than in L_2 <113>, most preferably 1.077 times higher than in L_2 <113>, where the proportion by mass of XOR in L_1 <115> and in L_2 <113> is more preferably in the range from 10% to 20% by weight, even more preferably 13% to 14% by weight.

[0145] An aqueous solution L_4 <116> of S is obtained at the outlet A_{KA} <106>, with a lower concentration of S in L_4 <116> than in L_3 <114>.

[0146] The concentration of the cation X in the aqueous solution L_3 <114> is preferably in the range of 3.5 to 5 mol/l, more preferably 4 mol/l. The concentration of the cation X in the aqueous solution L_4 <116> is more preferably 0.5 mol/l lower than that of the aqueous solution L_3 <114> used in each case.

[0147] In particular, the process according to the second aspect of the invention is conducted at a temperature of 20° C. to 70° C., preferably 35° C. to 65° C., more preferably 35° C. to 60° C., even more preferably 35° C. to 50° C., and at a pressure of 0.5 bar to 1.5 bar, preferably 0.9 bar to 1.1 bar, more preferably 1.0 bar.

[0148] In the course of performance of the process according to the invention, hydrogen is typically formed in the cathode chamber K_K <102>, which can be removed from the cell together with solution L_1 <115> via outlet A_{KK} <109>. The mixture of hydrogen and solution L_1 <115> can then, in a particular embodiment of the present invention, be separated by methods known to the person skilled in the art. When the alkali metal compound used is a halide, especially chloride, it is possible for chlorine or another halogen gas to form in the anode chamber K_A <101>, and this can be

removed from the cell together with solution L_4 <116> via outlet A_{KK} <106>. In addition, it is also possible for oxygen or/and carbon dioxide to form, which can likewise be removed. The mixture of chlorine, oxygen and/or CO_2 and solution L_4 <116> can then, in a particular embodiment of the present invention, be separated by methods known to the person skilled in the art. It is then likewise possible, after the chlorine, oxygen and/or CO_2 gases have been separated from solution L_4 <116>, to separate these by methods known to the person skilled in the art.

[0149] These results were surprising and unexpected in the light of the prior art. The process according to the invention protects the acid-labile solid-state electrolyte from corrosion without, as in the prior art, having to sacrifice alkoxide solution from the cathode space as buffer solution. Thus, the process according to the invention is more efficient than the procedure described in WO 2008/076327 A1, in which the product solution is used for the middle chamber, which reduces the overall conversion. In addition, the acid-labile solid-state electrolyte is stabilized in that the formation of a pH gradient is prevented on account of the internals <120>.

EXAMPLES

Comparative Example 1

[0150] Sodium methoxide (SM) was produced via a cathodic process, with supply of 20% by weight NaCl solution (in water) in the anode chamber and of 10% by weight methanolic SM solution in the cathode chamber. This electrolysis cell consisted of three chambers that corresponded to those shown in FIG. 1, except that the electrolysis cell did not have internals in the middle chamber, i.e. did not comprise the wire basket <122> with the glass beads <121> shown in FIG. 1. The connection between middle chamber and anode chamber was established by a hose mounted at the base of the electrolysis cell. The anode chamber and middle chamber were separated by a 2.83 cm^2 anion exchange membrane (Tokuyama AMX, ammonium groups on polymer). Cathode chamber and middle chamber were separated by a ceramic of the NaSICON type with an area of 2.83 cm^2 . The ceramic had a chemical composition of the formula $Na_{3.4}Zr_{2.0}Si_{2.4}P_{0.6}O_{12}$.

[0151] The anolyte was transferred through the middle chamber into the anode chamber. The flow rate of the anolyte was 1 l/h, that of the catholyte was 90 ml/h, and a current of 0.14 A was applied. The temperature was 35°C . The electrolysis was conducted for 500 hours at a constant voltage of 5 V. It was observed that a pH gradient developed in the middle chamber over a prolonged period, which is attributable to the migration of the ions to the electrodes in the course of the electrolysis and the spread of the protons formed in further reactions at the anode. This local increase in pH is undesirable since it can attack the solid-state electrolyte and can lead to corrosion and fracture of the solid-state electrolyte specifically in the case of very long periods of operation.

Comparative Example 2

[0152] Comparative Example 1 was repeated with a two-chamber cell comprising just one anode chamber and one cathode chamber, with the anode chamber separated from the cathode chamber by the ceramic of the NaSICON type. This electrolysis cell thus did not contain any middle cham-

ber. This is reflected in even faster corrosion of the ceramic compared to the comparative example 1, which leads to a rapid rise in the voltage curve. With a starting voltage value of <5 V, this rises to >20 V within 100 hours.

Inventive Example 1

[0153] Comparative Example 1 is repeated, with a basket <122> composed of wire framework with glass beads <121> placed in the middle chamber, said basket occupying the half of the middle chamber which faces the NASICON solid-state electrolyte. This arrangement interrupts the uniform flow of the electrolyte through the middle chamber, resulting in turbulence in the electrolyte. This makes it difficult for a pH gradient to build up during the electrolysis.

Inventive Example 2

[0154] Comparative Example 1 is repeated, with cone-shaped structures <123-1> and <123-2> secured to the NASICON ceramic or the diffusion barrier in the middle chamber K_M <103>.

[0155] This arrangement too interrupts the uniform flow of the electrolyte through the middle chamber, resulting in turbulence. This makes it difficult for a pH gradient to build up during the electrolysis.

Result

[0156] The use of a three-chamber cell according to the invention in the process according to the invention prevents the corrosion of the solid-state electrolyte, and at the same time there is no need to sacrifice alkali metal alkoxide product for the middle chamber and the voltage is kept constant. These advantages that are apparent from the comparison of the two Comparative Examples 1 and 2 underline the surprising effect of the present invention.

[0157] In addition, the alleviation or destruction of the pH gradient that builds up with progressive electrolysis by the vortexing and turbulence in the electrolyte in the middle chamber leads to extension of the lifetime of the electrolysis chamber. This gradient, specifically in the case of very long operating periods, can make the electrolysis even more difficult and lead to corrosion and ultimately fracture of the solid-state electrolyte. In the execution according to Inventive Examples 1 and 2, this pH gradient is destroyed, which, in addition to the advantages mentioned that are provided by a three-chamber cell over a two-chamber cell, further increases the stability of the solid-state electrolyte.

The invention claimed is:

1. An Electrolysis cell E <100> comprising at least one anode chamber K_A <101>, at least one cathode chamber K_K <102> and at least one interposed middle chamber K_M <103>,

wherein K_A <101> comprises an anodic electrode E_A <104> and an outlet A_{KA} <106>,

wherein K_K <102> comprises a cathodic electrode E_K <105>, an inlet Z_{KK} <107> and an outlet A_{KK} <109>,

wherein K_M <103> comprises an inlet Z_{KM} <108>, is divided from K_A <101> by a diffusion barrier D <110> and is divided from K_K <102> by an alkali metal cation-conducting solid-state electrolyte F_K <111>,

wherein K_M <103> and K_A <101> are connected to one another by a connection V_{AM} <112> through which liquid can be routed from K_M <103> into K_A <101>,

wherein the middle chamber K_M <103> comprises internals <120>, wherein the internals <120> are configured to lead to turbulence and vortexing in an electrolyte L_3 <114> that flows through the middle chamber K_M <103>.

2. The electrolysis cell E <100> according to claim 1, wherein the alkali metal ion-conducting solid-state electrolyte F_K <111> has a structure of the formula $M^I_{1+2w+x-y+z} M^{II}_x M^{III}_x Zr^{IV}_{2-w-x-y} M^V_y (SiO_4)_z (PO_4)_{3-z}$,

where M^I is selected from Na^+ and Li^+ ,

M^{II} is a divalent metal cation,

M^{III} is a trivalent metal cation,

M^V is a pentavalent metal cation,

the Roman indices I, II, III, IV, V indicate the oxidation numbers in which the respective metal cations exist, and w, x, y, z are real numbers, where $0 \leq x < 2, 0 \leq y < 2, 0 \leq w < 2, 0 \leq z < 3$,

and where w, x, y, z are chosen such that $1+2w+x-y+z \geq 0$ and $2-w-x-y \geq 0$.

3. The electrolysis cell E <100> according to claim 1, wherein the internals <120> are selected from the group consisting of trays, structured packings, unstructured packings.

4. The electrolysis cell E <100> according to claim 1, wherein the internals <120> comprise at least one material selected from rubber, plastic, glass, porcelain, metal.

5. The electrolysis cell E <100> according to claim 1, wherein the connection V_{AM} <112> is formed within the electrolysis cell E <100>.

6. The electrolysis cell E <100> according to claim 1, wherein the internals <120> account for a proportion ζ of 1% to 99% of the volume encompassed by the middle chamber K_M ,

wherein $\zeta = [(V_O - V_M)/V_O] * 100$,

and wherein V_O is the maximum volume of liquid that can be accommodated by the middle chamber K_M <103> if it does not comprise internals <120>,

and wherein V_M is the maximum volume of liquid that can be accommodated by the middle chamber K_M <103> if it comprises internals <120>.

7. The electrolysis cell E <100> according to claim 1, wherein internals <120> interrupt the direct pathway in the middle chamber K_M between inlet Z_{KM} <108> and connection V_{AM} <112> according to the thread test stated in the description.

8. The process for producing a solution L_1 <115> of an alkali metal alkoxide XOR in the alcohol ROH in an electrolysis cell E <100> according to claim 1,

wherein the process comprises the following steps (a), (b) and (c) that proceed simultaneously:

(a) a solution L_2 <113> comprising the alcohol ROH is routed through K_K <102>,

(b) a neutral or alkaline, aqueous solution L_3 <114> of a salt S comprising X as cation is routed through K_M <103>, then via V_{AM} <112>, then through K_A <101>,

(c) voltage is applied between E_A <104> and E_K <105>, which affords the solution L_1 <115> at the outlet A_{KK} <109>, with a higher concentration of XOR in L_1 <115> than in L_2 <113>,

and which affords an aqueous solution L_4 <116> of S at the outlet A_{KA} <106>, with a lower concentration of S in L_4 <116> than in L_3 <114>,

wherein X is an alkali metal cation and R is an alkyl radical having 1 to 4 carbon atoms.

9. The process according to claim 8, wherein X is selected from the group consisting of Li^+ , Na^+ , K^+ .

10. The process according to claim 8, wherein S is a halide, sulfate, sulfite, nitrate, hydrogencarbonate or carbonate of X.

11. The process according to claim 8, wherein R is selected from the group consisting of methyl and ethyl.

12. The process according to claim 8, wherein L_2 <113> comprises the alcohol ROH and an alkali metal alkoxide XOR.

13. The process according to claim 12, wherein the mass ratio of XOR to alcohol ROH in L_2 <113> is in the range from 1:100 to 1:5.

14. The process according to claim 12, wherein the concentration of XOR in L_1 <115> is 1.01 to 2.2 times higher than in L_2 <113>.

15. The process according to claim 8, which is performed at a temperature of 20 to 70° C. and a pressure of 0.5 to 1.5 bar.

16. The process according to claim 8, wherein the flow rate of the electrolyte L_3 <114> through the middle chamber K_M <103> is varied during the performance of step (b).

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