



(19) **United States**

(12) **Patent Application Publication**

**Stephan et al.**

(10) **Pub. No.: US 2004/0108220 A1**

(43) **Pub. Date: Jun. 10, 2004**

(54) **ELECTROCHEMICAL PRODUCTION OF NANOSCALE METAL (MIXED) OXIDES**

(30) **Foreign Application Priority Data**

Jan. 30, 2001 (DE)..... 101 04 302.3

(76) Inventors: **Hans-Oskar Stephan**, Duisburg (DE);  
**Christian Kropf**, Hilden (DE); **Rolf Hempelmann**, St. Ingbert (DE);  
**Andrea Dierstein**, Schiffweiler (DE);  
**Harald Natter**, Saarbruecken (DE)

**Publication Classification**

(51) **Int. Cl.<sup>7</sup>** ..... **C25B 1/00**  
(52) **U.S. Cl.** ..... **205/538**

Correspondence Address:  
**HENKEL CORPORATION**  
**THE TRIAD, SUITE 200**  
**2200 RENAISSANCE BLVD.**  
**GULPH MILLS, PA 19406 (US)**

(57) **ABSTRACT**

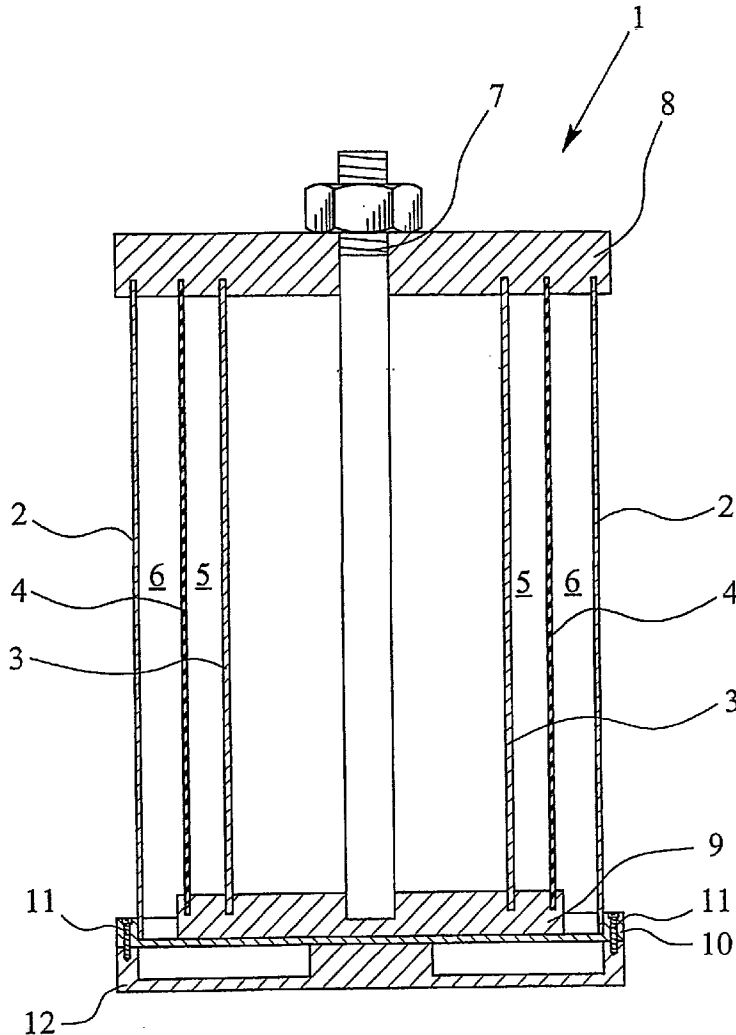
A process for the production of amorphous, crystalline, or mixed oxides of metals having mean particle diameters of 1 to 500 nm, by providing an electrolysis cell having a cathode in a cathode half-cell and an anode in an anode half cell, providing in the electrolysis cell a solution comprising ions of a metal or metals from which the oxide particles are to be formed dissolved in an organic electrolyte, and electrochemically reducing the metal ions at the cathode in the presence of an oxidizing agent while impeding or preventing passage of halogens from the anode half cell to the cathode half cell, to form the oxide or oxides.

(21) Appl. No.: **10/630,146**

(22) Filed: **Jul. 30, 2003**

**Related U.S. Application Data**

(63) Continuation of application No. PCT/EP02/00826, filed on Jan. 26, 2002.



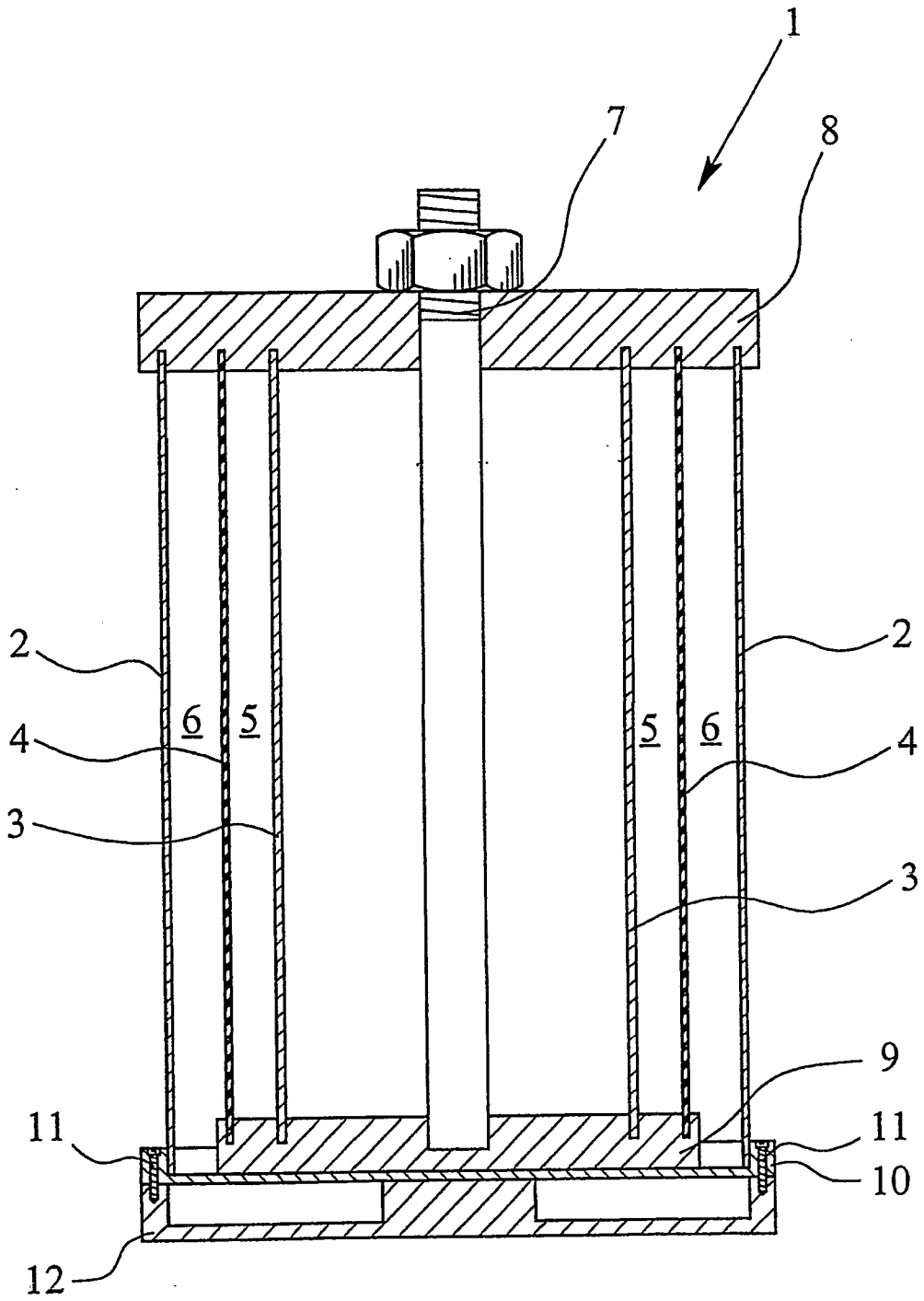


Fig. 1

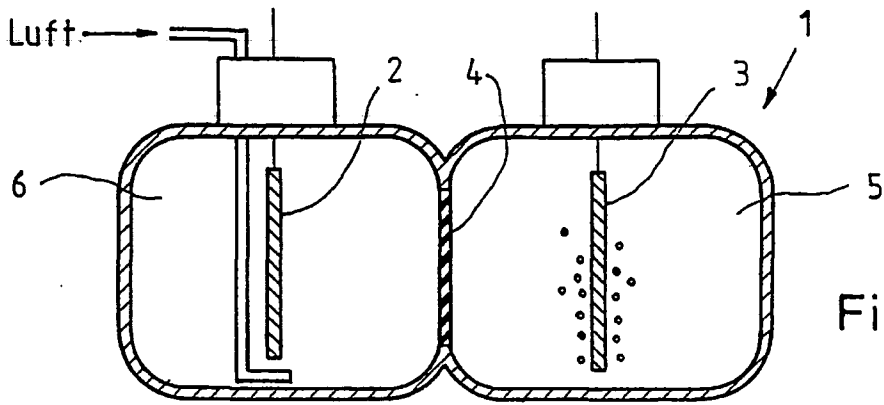


Fig. 2

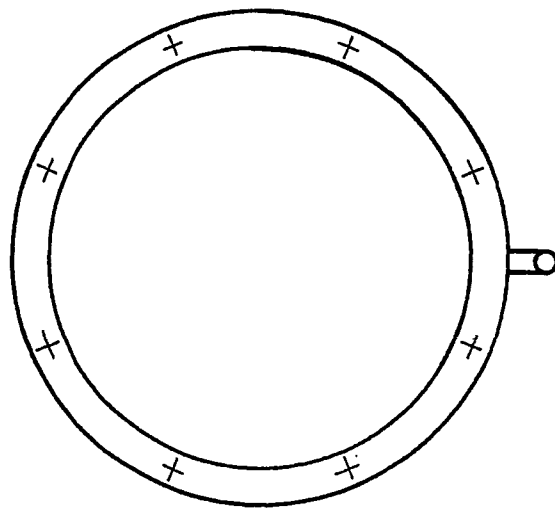


Fig. 3A

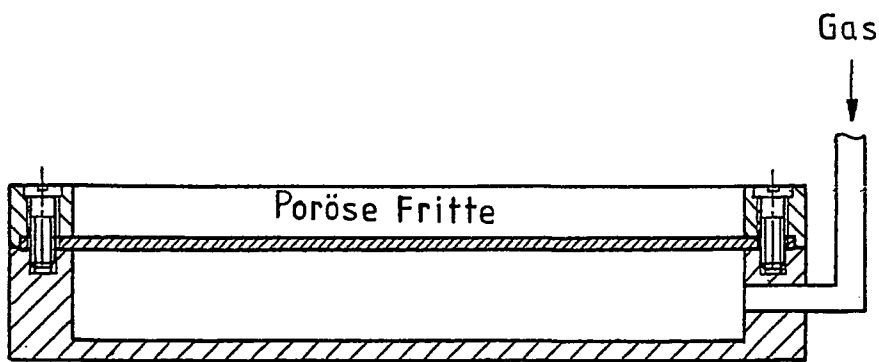


Fig. 3B

### ELECTROCHEMICAL PRODUCTION OF NANOSCALE METAL (MIXED) OXIDES

[0001] This invention relates to a process for the production of amorphous and/or crystalline oxides and mixed oxides of metals, more particularly metals of the third to fifth main group or the secondary groups, the (mixed) oxides thus produced having mean particle diameters in the nanometer range. In the context of the present invention, the "nanometer range" is understood in particular to be the range from about 1 nm to about 500 nm and preferably the range from about 1 nm to about 100 nm.

[0002] Metal oxides such as these may be used for various industrial applications, for example as dielectrics for miniaturized multilayer capacitors, as catalysts, as additives in paints and cosmetics, as additives in plastics to stabilize them against thermal or photochemical decomposition and/or to modify their dielectric and/or magnetic properties and as polishes.

[0003] Metal oxides with particle diameters in the nanometer range may be obtained, for example, by dissolving alkoxides of the metals in a water-immiscible solvent, preparing an emulsion of the resulting solution in water using suitable surfactants, the emulsified droplets of the solvent having diameters in the nanometer range, and hydrolyzing the metal alkoxides to the oxides. The disadvantages of this process lie in particular in the fact that the metal alkoxides are expensive starting materials, in the fact that emulsifiers also have to be used and in the fact that the preparation of the emulsion with droplet sizes in the nanometer range is a complicated process step.

[0004] It is also known that metal particles (not metal oxide particles!) with a particle size below 30 nm can be produced by cathodically reducing suitable metal salts in organic solvents or mixtures thereof with water in the presence of a stabilizer and optionally in the presence of a supporting electrolyte. Instead of dissolving metal salts in the electrolyte, the metal ions to be cathodically reduced can also be dissolved by using anodes of the corresponding metals which dissolve during the electrolysis. One such process is described in DE-A-44 43 392 and the corresponding EP-A-0 672 765.

[0005] In addition, DE-A-44 08 512 and the corresponding EP-A-0 672 765 describes a process for the electrolytic production of metal colloids in which one or more metals are anodically dissolved in aprotic organic solvents in the presence of a supporting electrolyte and cathodically reduced in the presence of stabilizers to colloidal metal solutions or redispersible metal colloid powders with a particle size below 30 nm. The supporting electrolyte and the stabilizer may be identical. If the cathodic reduction is carried out in the presence of suitable supports, the metal colloids are precipitated onto those supports.

[0006] In addition, according to Chemical Abstracts Report 110:65662, fine-particle zirconium oxide powder can be obtained by electrochemically producing a base in a solution of zirconyl nitrate, the zirconyl nitrate being hydrolyzed by the base with precipitation of hydrated zirconium oxide. Crystalline zirconium oxide can be obtained from the hydrated zirconium oxide by calcination.

[0007] According to Chemical Abstracts Report 114:31881, mixed oxides of iron, nickel and zinc can be

produced by electrochemically precipitating a hydroxide mixture of those metals from metal salt solutions and calcining the isolated hydroxides to the mixed oxides.

[0008] C. Pascal et al., "Electrochemical Synthesis for the Control of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> Nanoparticle Size. Morphology, Microstructure and Magnetic Behavior" in Chem. Mater. 1999, 11, pages 141-147, describe the electrochemical synthesis of nanoparticles of maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) in organic media by control of the current density and using cationic surfactants to stabilize the colloidal suspension of the particles obtained.

[0009] R. M. Nyffenegger et al., "A Hybrid Electrochemical/Chemical Synthesis of Zinc Oxide Nanoparticles and Optically Intrinsic Thin Films" in Chem. Mater. 1998, 10, pages 1120-1129, describe a chemical/electrochemical hybrid route for the production of zinc oxide nanoparticles and films, metallic zinc being electrochemically deposited onto a graphite electrode in a first step and the metallic zinc thus deposited being oxidized and dehydrated in a subsequent step.

[0010] E. P. Reddy et al., "Preparation and Characterization of Cobalt Oxide Nanosized Particles Obtained by an Electrochemical Method" in NanoStructured. Materials, Vol. 12, pages 61-64, 1999, describe a two-stage process for the electrochemical/chemical production of cobalt oxide particles in which, in a first stage, cobalt cations are precipitated in the presence of tetraalkyl ammonium salts as stable cobalt metal clusters which are then oxidized under the effect of oxygen to form nanoscale cobalt oxide particles which are stabilized with an ammonium salt.

[0011] S. Mahamuni et al., "Spectroscopic and Structural Characterization of Electrochemically Grown ZnO Quantum Dots" in J. Appl. Phys., Vol. 85, No. 5, pages 2861-2864, describe a process for the electrochemical synthesis of stable, hydroxide-free zinc oxide using a zinc sacrificial electrode which is reacted during electrolysis to form ZnO particles, the electrolysis being carried out under oxygen in acetonitrile and tetrahydrofuran in the presence of tetraoctyl ammonium bromide.

[0012] DE 198 408 42 A1 describes the electrochemical production of amorphous and crystalline nanoscale metal oxides and metal mixed oxides. In this process, metal ions are produced in situ, more particularly from a metal or alloy anode by electrochemical oxidation in an organic solvent, and the metal ions thus produced are reductively deposited as metal clusters onto the anode and converted in situ into the metal oxide under oxidizing conditions (for example purging with air). Additives and supporting electrolytes, preferably quaternary ammonium salts, present in the solution stabilize the nanostructure. Unfortunately, the process according to DE 198 408 42 A1 is attended by a number of problems. The price of certain metal plates as sacrificial electrode material (for example Mg, Zr, In, V) is very high and hence uneconomical. In addition, certain metals (for example Mn, Cr) are very difficult to produce as plates. For the deposition of mixed oxides, alloys have to be produced or several anodes have to be used which is both expensive and very time-consuming. In addition, where halides are used, the process according to DE 198 408 42 A1 is attended by the problem of anodic halogen deposition. The metal clusters formed are re-dissolved immediately after their formation by the chemically aggressive halogen and no product can be isolated. Accordingly, halogen-containing

compounds can only be used to a limited extent in this process. However, metal salt halides and the halogen compounds of the stabilizers (for example Dehyquart® A) are very low in price and often show extremely high solubility in organic media.

[0013] The problem addressed by the present invention was to provide a process for the production of amorphous and/or crystalline metal oxides or mixed oxides with mean particle diameters in the nanometer range. More particularly, this process would avoid the disadvantages of the prior art. It would even be possible to use metal halides and halogen-containing supporting electrolytes without any adverse effect on the formation of the metal oxides. In addition, the metal (mixed) oxides produced in particular would not be able to be contaminated by incorporation of anionic constituents emanating from the metal salts and/or supporting electrolytes.

[0014] Another problem addressed by the present invention was in particular to further develop the process described in DE 198 408 42 A1 to the extent that the disadvantages and problems mentioned above would be avoided.

[0015] Applicants have now surprisingly found that the problem stated above can be solved by the use of electrolysis cells with separate electrode compartments.

[0016] Accordingly, the present invention relates to a process for the production of amorphous and/or crystalline (mixed) oxides of metals, more particularly metals of the third to fifth main group or the secondary groups of the periodic system, with mean particle diameters of the (mixed) oxides in the range from 1 to 500 nm and more particularly 1 to 100 nm, characterized in that, in an electrolysis cell equipped with a cathode and an anode, ions dissolved in organic electrolyte of that metal or those metals of which the (mixed) oxide is to be produced are electrochemically reduced at the cathode in the presence of an oxidizing agent, the cathode compartment (cathode half-cell) and the anode compartment (anode half cell) being separated from one another by a porous partition or separating wall (diaphragm) which allows current to pass through, i.e. is permeable to cations and anions, but impedes and in particular prevents the passage of elemental halogen from the anode to the cathode compartment.

[0017] For example, a porous glass frit, more particularly with a pore diameter of about 1 to 4  $\mu\text{m}$ , may be used as the partition or separating wall. In addition, a polytetrafluoroethylene filter or a polytetrafluoroethylene membrane, more particularly with a pore diameter of about 1 to 4  $\mu\text{m}$ , may be used as the partition or separating wall. A porous polyethylene film or polyethylene disk (for example Vyon®, a material of low-pressure polyethylene), more particularly with a pore diameter of about 1 to 4  $\mu\text{m}$ , may also be used as the partition or separating wall. Equally, a proton-conducting membrane, more particularly a perfluorinated ion exchanger membrane (for example Nafion® from DuPont or Aldrich), preferably with a pore diameter of about 1 to 4  $\mu\text{m}$ , may be used as the partition or separating wall. The Nafion® membrane is a membrane with a Teflon-like structure. The advantage of Nafion® membranes for example lies in their high chemical resistance, their high ion conductivity and the high halogen retention capacity. In addition, these films are

very easy to process in a thickness of 128  $\mu\text{m}$  and thus provide for uncomplicated production of the electrolysis cells.

[0018] Through the separation of the electrode compartments by the diaphragm used in accordance with the invention, electrical conductivity is maintained but no halide is able to enter the cathode compartment.

[0019] In the process according to the invention, the mean particle diameter of the (mixed) oxides can be adjusted by varying the temperature of the electrolyte, the electrical voltage or current intensity and through the nature of the supporting electrolyte optionally used. The process according to the invention is preferably carried out in such a way that the metal oxides obtained have mean particle diameters in the range from 1 to about 500 nm and preferably in the range from about 1 to about 100 nm.

[0020] Using the process according to the invention, it is possible in particular to produce metal oxides which do not react with moisture to form hydroxides at a temperature below about 100° C. Accordingly, the process according to the invention is not suitable for the production of oxides and mixed oxides of alkali or alkaline earth metals. It is also particularly suitable for the production of oxides of metals which are oxidized by atmospheric oxygen at temperatures below about 100° C. Where metals such as these are used, the process according to the invention may be carried out at temperatures below 100° C. using air as the oxidizing agent. This enables the process to be carried out in an uncomplicated manner. The process according to the invention is particularly suitable for the production of amorphous and/or crystalline oxides and mixed oxides of Ti, Zr, Cr, Mo, Fe, Co, Ni, Pb, In, Sn and/or Al.

[0021] The organic electrolyte used is preferably a substance which is liquid at temperatures in the range from about -78° C. to about +260° C. at normal pressure. In one particularly preferred embodiment, a substance which is liquid at temperatures in the range from about 0 to about 60° C. at normal pressure is used. The organic electrolyte is preferably selected from alcohols (for example isopropanol or n-propanol) or polyalcohols (for example glycerol or polyglycols) or mixtures and derivatives thereof, ketones, ethers (for example tetrahydrofuran or diethyl ether), nitrites, organic carbonates (for example propylene carbonate or diethyl carbonate) and aromatic compounds, those which are liquid at temperatures in the ranges mentioned being preferred. Other particularly suitable electrolytes are tetrahydrofuran, acetone, acetonitrile, toluene and mixtures thereof with alcohols.

[0022] Depending on the metal (mixed) oxide to be produced, it can be favorable if the electrolyte contains small quantities of water. For example, the water content of the organic electrolyte may be in the range from about 0.01 to about 2% by weight and, more particularly, is in the range from about 0.05 to about 1% by weight, the percentages by weight being based on the total quantity of organic electrolyte and water.

[0023] Should the electrolyte not of itself have an adequate electrical conductivity or acquire an adequate electrical conductivity by dissolution in salts of the metals whose (mixed) oxides are to be produced, it is advisable to dissolve a supporting electrolyte in the electrolyte. The usual

supporting electrolytes which are normally used to give the electrolytes mentioned an electrical conductivity sufficient for electrochemical processes may be employed. Suitable supporting electrolytes are, for example, electrolyte-soluble hexafluorophosphates, sulfonates, acetyl acetates, carboxylates and in particular quaternary phosphonium and/or ammonium salts with organic groups at the phosphorus or at the nitrogen. Preferred supporting electrolytes are quaternary ammonium compounds which bear aryl and/or alkyl groups at the nitrogen and which are preferably present as halides. One example of a particularly suitable supporting electrolyte is tetrabutyl ammonium bromide. If necessary, these supporting electrolytes may be used together with surfactants which stabilize the metal oxide particles produced. The surfactants are selected in particular from the entire class of surfactants, the following compounds preferably being used: fatty alcohols, fatty alcohol ethoxylates, polyoxyethylene carboxylic acids and/or fatty acid ethoxylates.

[0024] The process according to the invention is preferably carried out in a temperature range in which the supporting electrolyte is sufficiently soluble in the organic electrolyte. The process according to the invention is preferably carried out in such a way that the organic electrolyte has a temperature in the range from about 30° C. to about 50° C. If tetrahydrofuran is used as the electrolyte and tetrabutyl ammonium bromide as the supporting electrolyte, the process is preferably carried out at temperatures above 35° C., for example in the range from 35° C. to 40° C.

[0025] The supporting electrolytes have the additional effect that they protect the oxide particles formed against agglomeration. A very narrow particle size distribution can be obtained in this way. If no importance is attached to a narrow particle size distribution, there is no need to add the supporting electrolytes providing the electrolyte has an adequate electrical conductivity from the dissolved salts of the metal to be precipitated as oxide.

[0026] According to the invention, the metal (mixed) oxides are formed by electrochemical reduction of the ions of the metals at a cathode in the presence of an oxidizing agent. The easiest oxidizing agent to use is oxygen or air. Accordingly, oxygen or air is preferably used. In a preferred embodiment, therefore, the process is carried out by introducing air into the electrolyte during the electrochemical reduction of the metal ions. Accordingly, the metal particles deposited in the first stage are preferably oxidized by atmospheric oxygen. To this end, the air is introduced in the form of small bubbles which, on the one hand, provide for fine distribution of the oxidizing agent oxygen in the cathode compartment and, on the other hand, ensure through the constant mixing of the electrolyte that no solid metal oxide layer is formed on the cathode, but instead that the metal oxide particles are flushed from the cathode and dispersed in the electrolyte. A device for introducing air in the form of small bubbles is shown in FIG. 3. In this device, compressed air is passed through a flat frit material. Vyon® (pore diameter 5 to 40 μm), porous Teflon® and even ceramic frits, for example, may be used for this purpose. The frits are between 2 and 5 mm in thickness. The frit may be screwed by a ring onto a wall (see FIG. 3 in particular). The seal between the tank and the frit may be provided by the frit material itself. In the case of ceramic frits, it is advisable for example to use a rubber seal. The body of this device may

be made, for example, of a solvent-resistant plastic, such as PEK, PVC or Teflon®. The device may also be made of metal. To support oxidation in the case of highly surface-active additives, such as fatty alcohols for example, pure oxygen may be added (up to ca. 70% by volume). If desired, oxygen-enriched air or substantially pure oxygen may also be introduced into the electrolyte. If highly inflammable electrolytes are used, it may be advisable for reasons of operational safety to enrich the air with nitrogen to such an extent that the oxygen partial pressure remains below the value required for ignition of the gas mixture. Other suitable but less preferred oxidizing agents are hydrogen peroxide, organic or inorganic peroxy compounds or oxo anions of the halogens chlorine, bromine or iodine where the halogen has an oxidation number of +1 to +5. However, if stronger oxidizing agents than atmospheric oxygen are used, it is important to ensure that there is no peroxide formation with the electrolyte.

[0027] The electrical d.c. voltage between cathode and anode is preferably adjusted so that a current density of 0.05 to 10 mA/cm<sup>2</sup>, based on the anode area, and preferably in the range from 1 to 5 mA/cm<sup>2</sup> is obtained. Given a sufficiently conductive electrolyte, this can be achieved by applying a d.c. voltage of about 1 to about 100 volts between the cathode and anode.

[0028] In a preferred embodiment, the electrolyte is vigorously agitated throughout the process according to the invention. This can be done, for example, by stirring the electrolyte. In addition or alternatively, the electrolyte may be ultrasonicated for this purpose. It is also possible, particularly where atmospheric oxygen is used as the oxidizing agent, to use the gas stream to be introduced in the form of small gas bubbles for convection of the electrolyte. The advantage of electrolyte agitation and/or ultrasonication is that the metal oxides formed do not adhere to the cathode, i.e. do not cover it with an insulating layer.

[0029] The ions of the metal or metals whose oxides or mixed oxides are to be produced can enter the electrolyte in various ways.

[0030] In a preferred embodiment, the process according to the invention may be carried out by using an inert anode and dissolving in the electrolyte a salt of the metal or salts of the metals of which the oxide or mixed oxide is to be produced. In this case, the salts selected must of course be sufficiently soluble in the electrolyte used. The metal salts used may generally be halides (preferably fluorides, chlorides, bromides and iodides), nitrates, acetates, sulfonates, carboxylates and hexafluorophosphates of the metals and mixtures thereof. Where tetrahydrofuran, for example, is used as the electrolyte, chlorides or nitrates of the particular metals, for example, are generally suitable. In this embodiment, mixed oxides may also be produced where metal salt mixtures are used. A material which is inert under the electrolysis conditions selected is preferably used as the cathode material and optionally the anode material. In view of the aggressive conditions in the anode compartment, chemically resistant anode materials are generally used. Suitable electrode materials are, for example, electrodes of platinum or other platinum metals, gold, niobium, tantalum, tungsten, graphite or glassy carbon. The materials are equally suitable as cathode and anode materials.

[0031] Another particular embodiment for the production of mixed oxides is a "hybrid process" between the process

using a sacrificial anode according to DE 198 408 42 A1 and the "salt route" previously described. This embodiment may be used in particular in cases where, in the production of mixed oxides, solubility problems exist for a corresponding metal salt component. In addition, doping material could be introduced into deposited products in this way. In this special embodiment, the process according to the invention—in the production of mixed oxides of at least two metals—may be carried out, for example, by producing the metal ions dissolved in the electrolyte by dissolving a salt of one metal in the electrolyte and using an anode (sacrificial anode) containing the other metal. For example, the anode used may contain or consist of the metal whose oxide is to be produced and may dissolve anodically during the production of the oxides. Equally, the anode used may be an anode of an inert material coated beforehand with the metal whose oxide is to be produced. In the latter case, the corresponding metal separates anodically from the anode during the electrochemical production of the metal oxide.

[0032] The oxides or the mixed oxides are obtained in X-ray amorphous or crystalline form, depending on the metal and the electrolysis conditions. Accordingly, they show either an X-ray diffractogram which resembles that of a liquid and has only a few broad maxima (X-ray amorphous) or which consists of individual clearly contrasting X-ray reflexes (X-ray crystalline). The X-ray amorphous or X-ray crystalline metal oxides obtained are separated from the electrolyte either continuously or in batches, for example by continuous or discontinuous filtration or centrifugation. If necessary, the metal oxides separated from the electrolyte are washed, preferably with the organic solvent used as electrolyte, optionally at elevated temperature, in order to remove any salt residues and stabilizer residues present. The metal oxides are then dried, for example at a temperature of 100° C.

[0033] If it is intended to produce crystalline metal oxides or mixed oxides and if they do not accumulate in the desired form during the electrolysis process, the metal (mixed) oxides separated from the electrolyte may be thermally aftertreated. For example, they may be converted into an X-ray crystalline form by calcination at a temperature in the range from about 300 to about 1200° C. and more particularly at a temperature in the range from about 400 to about 1,000° C. The calcination time will depend on the rate at which the amorphous (mixed) oxides are converted into the crystalline (mixed) oxides and may be, for example, between about 5 minutes and about 4 hours. Depending on the metal (mixed oxide selected, the size of the crystallites may increase with increasing calcination time. Alternatively, the amorphous samples may be subjected to a hydrothermal treatment. To this end, a solvent, preferably water, is added to the samples which are then treated for a few hours in a closed vessel under autogenous pressure and at a temperature of 100 to 250° C. The organic constituents adhering to the particles are removed by this procedure. At the same time, the growth of the nanoscale primary particles is seriously restricted and preferably avoided.

[0034] FIGS. 1 and 2 are each sections through an arrangement 1 suitable for carrying out the process according to the invention. In this particular embodiment, the electrolysis cell 1—as shown in FIG. 1—is in the form of a system of concentric tubes. The outer tube 2, which consists for example of 0.5 mm thick stain steel plate, is

preferably the cathode. The middle tube 4 is formed by a cation-conducting membrane, for example a Nafion® membrane. The outer tube 2 and the middle tube 4 with the membrane delimit the space of the cathode half cell 6. The counter-electrode 3, for example an electrode of platinum, titanium or graphite which is preferably used as the anode, represents the inner of the concentric tubes. The inner tube 3 (anode) and the membrane layer 4 delimit the space of the anode half cell 5. The individual tubes 2 (cathode), 4 (membrane), 3 (anode) are held in place by mutually opposite holders 8, 9 and 10 which are held together by a fixing element 7, for example in the form of a screw, for example of an inert material, such as a suitable plastic. The above-described arrangement for carrying out the process according to the invention may be connected to a suitable current and voltage source. FIG. 1 shows a particular embodiment of an arrangement for carrying out the process according to the invention. The process according to the invention is not of course confined to that particular embodiment. The expert will know of numerous possible modifications and variants as to how the anode half cell and the cathode half cell can be separated from one another by a diaphragm without departing from the scope of the present invention (see FIG. 2 for example).

[0035] The process according to the invention has a number of advantages over the prior art.

[0036] The process according to the invention provides for the relatively simple production of nanoscale, amorphous and crystalline metal oxides and mixed oxides from metal salt solutions. In contrast to the process according to DE 198 408 42 A1, the metal ions required do not have to be formed in situ from metal plates during the process, but may be directly added to the starting electrolyte as metal salt. Where halide salts (metal salts and/or supporting electrolytes) are used, the problem of halogen deposition where the metal clusters formed are re-dissolved immediately after their formation does not arise. Accordingly, metal salt halides and the halogen compounds of the stabilizers (for example Dehyquart® A), which are often very low in price and generally show extremely high solubility in organic media, may readily be used. In addition, contamination of the metal (mixed) oxides produced by the incorporation of anionic constituents emanating from the metal salts and/or supporting electrolytes can be avoided because they remain in the anode compartment.

[0037] Further embodiments and variations of the present invention will be readily apparent to the expert on reading the specification and could be put into practice without departing from the scope of the present invention.

[0038] The following Examples are intended to illustrate the invention without limiting it in any way.

#### EXAMPLES

[0039] In the following Examples, solutions of various metal salts or mixtures thereof were electrolyzed under the particular process conditions according to the invention indicated. The arrangement shown in FIG. 2 was used for the tests. The results obtained are as follows:

## Example 1

[0040]

---

Electrolyte cathode compartment:	isopropanol, tetrabutyl ammonium bromide (TBAB) (0.1 M), 1 g ZnCl <sub>2</sub>
Electrolyte anode compartment:	isopropanol, TBAB (0.1 M)
Electrodes:	2 × Pt
Current density:	3 mA/cm <sup>2</sup>
Diaphragm material:	porous glass frit
Product:	ZnO, crystalline

---

## Example 2

[0041]

---

Electrolyte cathode compartment:	isopropanol, TBAB (0.1 M), 1 g
Electrolyte anode compartment:	MnCl <sub>2</sub> isopropanol, TBAB (0.1 M)
Electrodes:	2 × Pt
Current density:	3 mA/cm <sup>2</sup>
Diaphragm material:	porous glass frit
Product:	γ-Mn <sub>3</sub> O <sub>4</sub> (tetragonal), crystalline

---

## Example 3

[0042]

---

Electrolyte cathode compartment:	200 ml n-propanol, TBAB (0.1 M), 2.0 g NiCl <sub>2</sub> × 6H <sub>2</sub> O
Electrolyte anode compartment:	200 ml n-propanol, TBAB (0.1 M)
Electrodes:	2 × Pt
Current density:	3 mA/cm <sup>2</sup>
Diaphragm material:	porous glass frit
Product:	X-ray amorphous, light green
Calcination (45 mins./300° C.):	NiO, black

---

## Example 4

[0043]

---

Electrolyte cathode compartment:	200 ml n-propanol, TBAB (0.1 M), 1.5 g FeCl <sub>2</sub>
Electrolyte anode compartment:	200 ml n-propanol, TBAB (0.1 M)
Electrodes:	2 × Pt
Current density:	3 mA/cm <sup>2</sup>
Diaphragm material:	porous glass frit
Product:	X-ray amorphous
Calcination (15 mins./500° C.):	α-Fe <sub>2</sub> O <sub>3</sub> + γ-Fe <sub>2</sub> O <sub>3</sub>

---

## Example 5

[0044]

---

Electrolyte cathode compartment:	200 ml n-propanol, TBAB (0.1 M), 1.5 g CoCl <sub>2</sub> × 6H <sub>2</sub> O
Electrolyte anode compartment:	200 ml n-propanol, TBAB (0.1 M)
Electrodes:	2 × Pt
Current density:	3 mA/cm <sup>2</sup>

---

-continued

---

Diaphragm material:	porous glass frit
Product:	X-ray amorphous
Calcination (35 mins./500° C.):	Co <sub>3</sub> O <sub>4</sub>

---

## Example 6

[0045]

---

Electrolyte cathode compartment:	200 ml n-propanol, cetylmethyl ammonium chloride (Dehyquart A) (0.1 M), 1.5 g FeCl <sub>3</sub> , 0.6 g CoCl <sub>2</sub> × 6H <sub>2</sub> O (Co:Fe = 1:2)
Electrolyte anode compartment:	200 ml n-propanol, Dehyquart A (0.1 M)
Electrodes:	2 × Pt
Current density:	3 mA/cm <sup>2</sup>
Diaphragm material:	porous glass frit
Product:	X-ray amorphous
Calcination (30 mins./500° C.):	CoFe <sub>2</sub> O <sub>4</sub>

---

## Example 7

[0046]

---

Electrolyte cathode compartment:	200 ml n-propanol, TBAB (0.1 M), SnCl <sub>2</sub> (0.015 M)
Electrolyte anode compartment:	200 ml n-propanol, TBAB (0.1 M)
Electrodes:	In anode, stainless steel cathode
Current density:	3 mA/cm <sup>2</sup>
Diaphragm material:	porous glass frit
Product:	X-ray amorphous
Calcination (30 mins./700° C.):	In <sub>2</sub> O <sub>3</sub> + SnO <sub>2</sub>

---

## Example 8

[0047]

---

Electrolyte cathode compartment:	n-propanol, TBAB (0.1 M); ZnCl <sub>2</sub> (0.05 M)
Electrolyte anode compartment:	n-propanol, TBAB (0.1 M)
Cathode:	stainless steel
Anode:	graphite
Current density:	1 mA/cm <sup>2</sup>
Diaphragm material:	Vyon ® F
Product:	white crystalline ZnO

---

## Example 9

[0048]

---

Electrolyte cathode compartment:	isopropanol, TBAB (0.1 M); MnCl <sub>2</sub> (0.05 M)
Electrolyte anode compartment:	isopropanol, TBAB (0.1 M)
Electrodes:	2 × Pt
Current density:	3 mA/cm <sup>2</sup>
Diaphragm material:	Teflon ®
Product:	crystalline, γ-Mn <sub>3</sub> O <sub>4</sub> (tetragonal)

---

## Example 10

[0049]

Electrolyte cathode compartment:	1-propanol, Dehyquart A (0.05 M), 6.8 g ZnCl <sub>2</sub> (0.1 M), CaCl <sub>2</sub> (0.1 M)
Electrolyte anode compartment:	1-propanol, Dehyquart A (0.05 M) CaCl <sub>2</sub> (0.1 M)
Electrodes:	graphite anode, platinized Ti cathode
Current density:	3 mA/cm <sup>2</sup>
Diaphragm material:	Nafion®
Product:	crystalline ZnO

## Example 11

[0050]

Electrolyte cathode compartment:	1-propanol, Dehyquart A (0.1 M), FeCl <sub>3</sub> (anhydrous)
Electrolyte anode compartment:	1-propanol, Dehyquart A (0.1 M)
Electrodes:	graphite anode, stainless steel cathode
Current density:	0.5 mA/cm <sup>2</sup>
Diaphragm material:	Nafion®
Product:	amorphous
Calcination (30 mins./500° C.):	crystalline: $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> + $\gamma$ -Fe <sub>2</sub> O <sub>3</sub>

## Example 12

[0051]

Electrolyte cathode compartment:	1-propanol, TBAB (0.1 M), CoCl <sub>2</sub> × 6H <sub>2</sub> O (0.025 M)
Electrolyte anode compartment:	1-propanol, TBAB (0.1 M)
Electrodes:	graphite anode, stainless steel cathode
Current density:	0.5 mA/cm <sup>2</sup>
Diaphragm material:	Nafion®
Product:	amorphous
Calcination (30 mins./500° C.):	crystalline: Co <sub>3</sub> O <sub>4</sub>

1. A process for the production of amorphous and/or crystalline (mixed) oxides of metals, more particularly metals of the third to fifth main group or the secondary groups of the periodic system, with mean particle diameters of the (mixed) oxides in the range from 1 to 500 nm and more particularly 1 to 100 nm, characterized in that, in an electrolysis cell equipped with a cathode and an anode, ions dissolved in organic electrolyte of that metal or those metals of which the (mixed) oxide is to be produced are electrochemically reduced at the cathode in the presence of an oxidizing agent, characterized in that the cathode compartment (cathode half-cell) and the anode compartment (anode half cell) are separated from one another by a porous partition or separating wall (diaphragm) which allows current to pass through, i.e. is permeable to cations and anions, but impedes and in particular prevents the passage of elemental halogen from the anode to the cathode compartment.

2. A process as claimed in claim 1, characterized in that the porous partition or separating wall in particular has a high halogen retention capacity.

3. A process as claimed in claim 1 or 2, characterized in that the porous partition or separating wall is a porous glass frit, more particularly with a pore diameter of about 1 to 4  $\mu$ m.

4. A process as claimed in claim 1 or 2, characterized in that the porous partition or separation wall is a polytetrafluoroethylene filter or a polytetrafluoroethylene membrane or a porous polyethylene film or polyethylene disk, more particularly with a pore diameter of about 1 to 4  $\mu$ m.

5. A process as claimed in claim 1 or 2, characterized in that the porous partition or separation wall is a proton-conducting membrane, preferably with a pore diameter of about 1 to 4  $\mu$ m.

6. A process as claimed in claim 5, characterized in that the proton-conducting ion exchanger membrane is in particular a perfluorinated ion exchanger membrane, preferably with a pore diameter of about 1 to 4  $\mu$ m.

7. A process as claimed in any of claims 1 to 6, characterized in that organic electrolyte used is a substance which is liquid at temperatures in the range from about -78° C. to about +260° C. and more particularly in the range from about 0° C. to about 60° C. at normal pressure and is preferably selected from the group consisting of ketones, alcohols and polyalcohols, ethers, nitrites and aromatic compounds.

8. A process as claimed in claim 7, characterized in that the organic electrolyte is selected from the group consisting of n-propanol, i-propanol, glycerol and mixtures thereof with acetone, tetrahydrofuran, acetonitrile and toluene.

9. A process as claimed in any of claims 1 to 8, characterized in that the organic electrolyte additionally contains small quantities of water, more particularly about 0.01 to about 2% by weight and preferably about 0.05 to about 1% by weight, based on the total quantity of the organic electrolyte and water.

10. A process as claimed in any of claims 1 to 9, characterized in that the organic electrolyte additionally contains a dissolved supporting electrolyte which may be selected in particular from the group consisting of electrolyte-soluble hexafluorophosphates, sulfonates, acetyl acetates, carboxylates and quaternary phosphonium and/or ammonium salts, more particularly with organic groups at the phosphorus and/or nitrogen, the supporting electrolyte being used together with surfactants which stabilize the metal oxide particles produced and preferably being selected from the entire class of surfactants, the following compounds being particularly preferred: fatty alcohols, fatty alcohol ethoxylates, polyoxyethylene carboxylic acids and/or fatty acid ethoxylates.

11. A process as claimed in claim 10, characterized in that the supporting electrolyte used is a quaternary ammonium compound which may optionally carry one or more aryl and/or alkyl groups at the nitrogen and which is preferably present as a halide, such as tetrabutyl ammonium bromide.

12. A process as claimed in any of claims 1 to 11, characterized in that the organic electrolyte has a temperature of 30 to 120° C.

13. A process as claimed in one or more of claims 1 to 12, characterized in that the oxidizing agent is selected from the group consisting of oxygen, hydrogen peroxide, peroxy compounds and oxo anions of the halogens chlorine, bromine or iodine where the halogen in particular has an oxidation number of +1 to +5.

**14.** A process as claimed in claim 13, characterized in that the oxidizing agent is air (atmospheric oxygen), the oxidizing agent preferably being supplied to the reaction system by introduction of air into the electrolyte solution.

**15.** A process as claimed in any of claims 1 to 14, characterized in that the electrical d.c. voltage between cathode and anode is preferably adjusted so that a current density of 0.05 to 10 mA/cm<sup>2</sup>, based on the anode area, and preferably in the range from 1 to 5 mA/cm<sup>2</sup>, is obtained.

**16.** A process as claimed in claim 15, characterized in that an electrical d.c. voltage of 1 to 100 volts is applied between cathode and anode.

**17.** A process as claimed in any of claims 1 to 16, characterized in that the electrolyte is agitated, more particularly by stirring, introduction of a gas and/or ultrasonication.

**18.** A process as claimed in any of claims 1 to 17, characterized in that the anode and/or cathode material is a material which is inert under the selected electrolysis conditions and which is selected in particular from the group consisting of platinum and other platinum metals, gold, niobium, tantalum, tungsten, graphite and glassy carbon.

**19.** A process as claimed in any of claims 1 to 18, characterized in that the metal ions dissolved in the electrolyte are produced by dissolving in the electrolyte a salt of the metal or salts of those metals whose oxide or mixed oxide is to be produced.

**20.** A process as claimed in claim 19, characterized in that a halide, nitrate, acetate, sulfonate, carboxylate or hexafluorophosphate is used as the metal salt.

**21.** A process as claimed in any of claims 1 to 20, characterized in that, in the production of mixed oxides of at least two metals, the metal ions dissolved in the electrolyte are produced by dissolving a salt of one metal in the electrolyte and using an anode containing the other metal as a sacrificial anode.

**22.** A process as claimed in any of claims 1 to 21, characterized in that the metal (mixed) oxide formed is separated from the electrolyte and dried.

**23.** A process as claimed in claim 22, characterized in that the dried metal (mixed) oxide is subsequently calcined, more particularly at a temperature in the range from about 300 to about 1200° C. and preferably at a temperature in the range from about 400 to about 1,000° C., or subjected to a hydrothermal treatment.

**24.** The use of the process claimed in any of claims 1 to 23 for the production of amorphous and/or crystalline oxides and mixed oxides of metals of the third to fifth main group or the secondary groups of the periodic system, more particularly of titanium, zirconium, chromium, molybdenum, iron, cobalt, nickel, indium, tin, lead and/or aluminium.

\* \* \* \* \*