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(54) AN ELECTROCHEMICAL PROCESS FOR PREPARING A COMPOUND COMPRISING A METAL OR METALLOID AND A PEROXIDE, IONIC OR RADICAL SPECIES

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(57) **ABSTRACT**

An electrochemical process is for recovering a metal element or a metalloid element or a mixture of two or more thereof from at least one water soluble precursor compound containing the metal element or a metalloid element or two or more thereof, in the form of one or more nano particles, in particular nano crystals of at least one reaction product. The process includes supplying the water soluble precursor compound to a water-based catholyte of a cathode compartment of an electrochemical cell, equipped with a cathode containing a gas diffusion electrode, adjusting the pH of the catholyte, supplying at least one oxidant gas to the gas diffusion electrode, and subjecting the cathode to an electrochemical potential to cause reduction of the at least one oxidant gas.

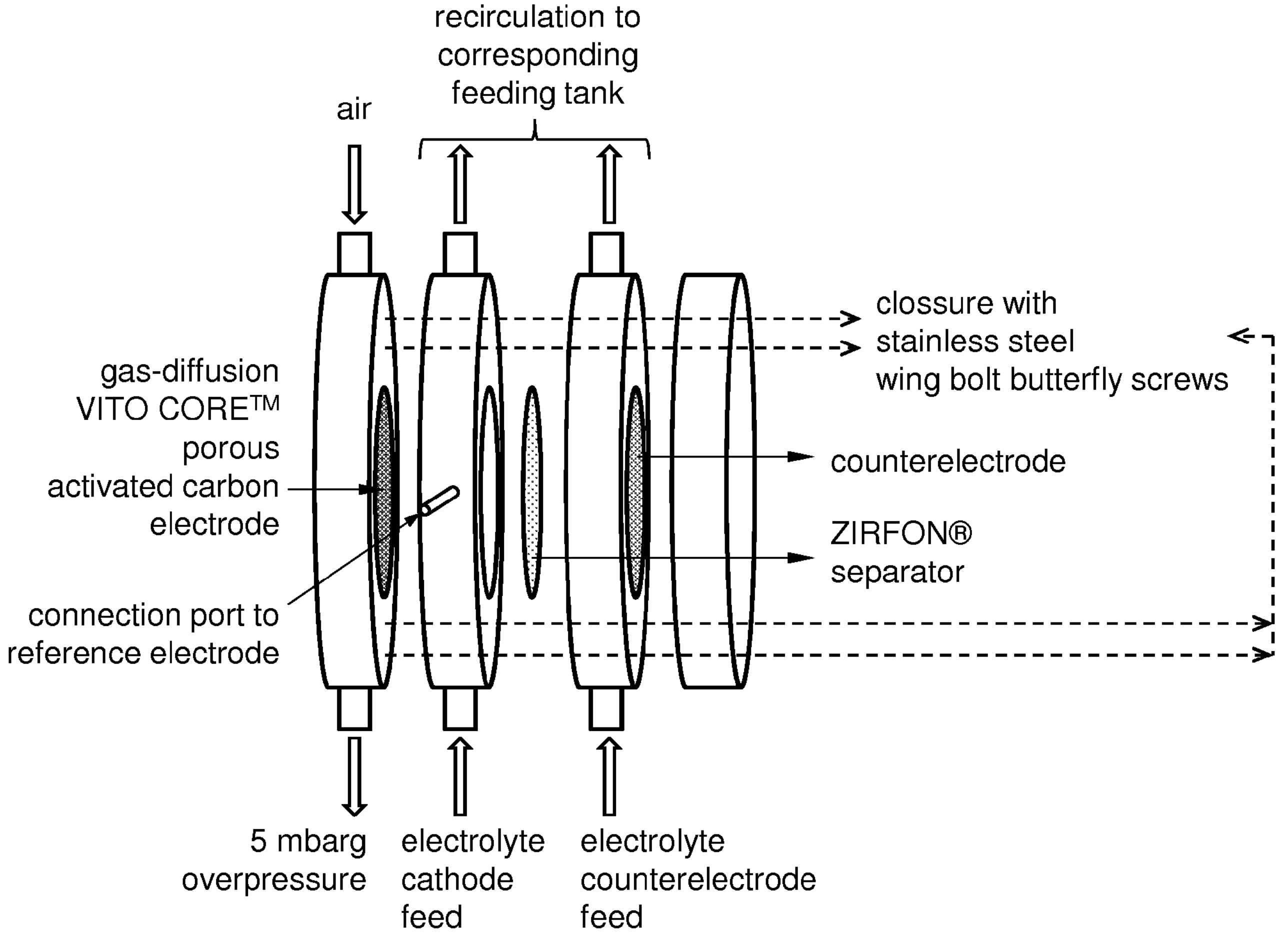

air
recirculation to corresponding feeding tank
gas-diffusion VITO CORE™ porous activated carbon electrode
connection port to reference electrode
closssure with stainless steel wing bolt butterfly screws
counterelectrode
ZIRFON® separator
5 mbarg overpressure
electrolyte cathode feed
electrolyte counterelectrode feed

Fig. 1a

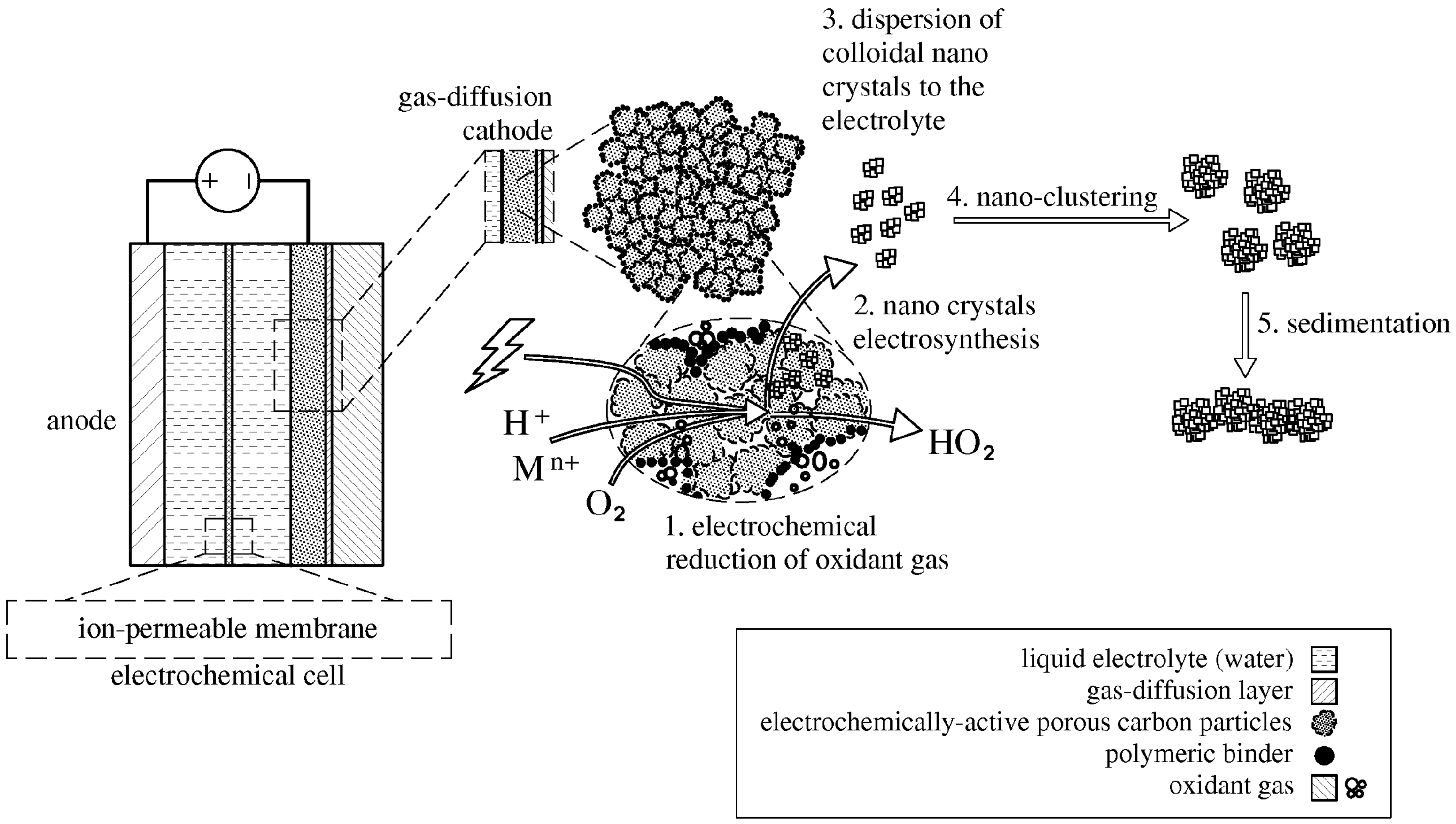

gas-diffusion cathode
anode
ion-permeable membrane
electrochemical cell
3. dispersion of colloidal nano crystals to the electrolyte
4. nano-clustering
2. nano crystals electrosynthesis
5. sedimentation
H⁺
Mⁿ⁺
O₂
HO₂
1. electrochemical reduction of oxidant gas
liquid electrolyte (water)
gas-diffusion layer
electrochemically-active porous carbon particles
polymeric binder
oxidant gas

Fig. 1b

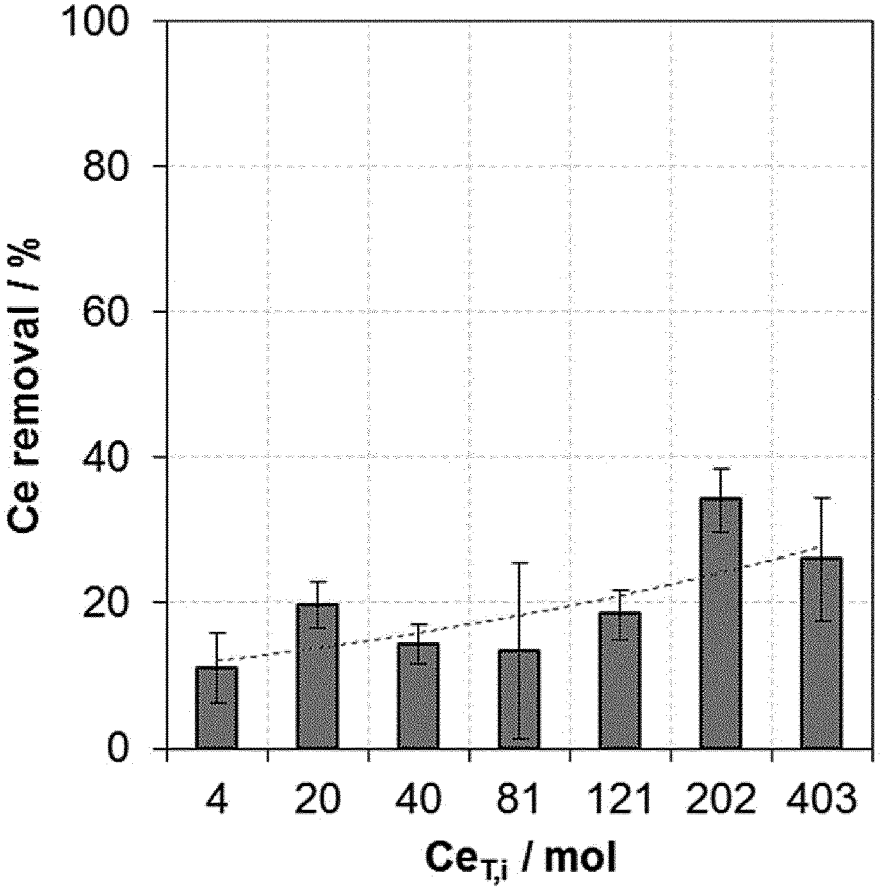


Fig. 2

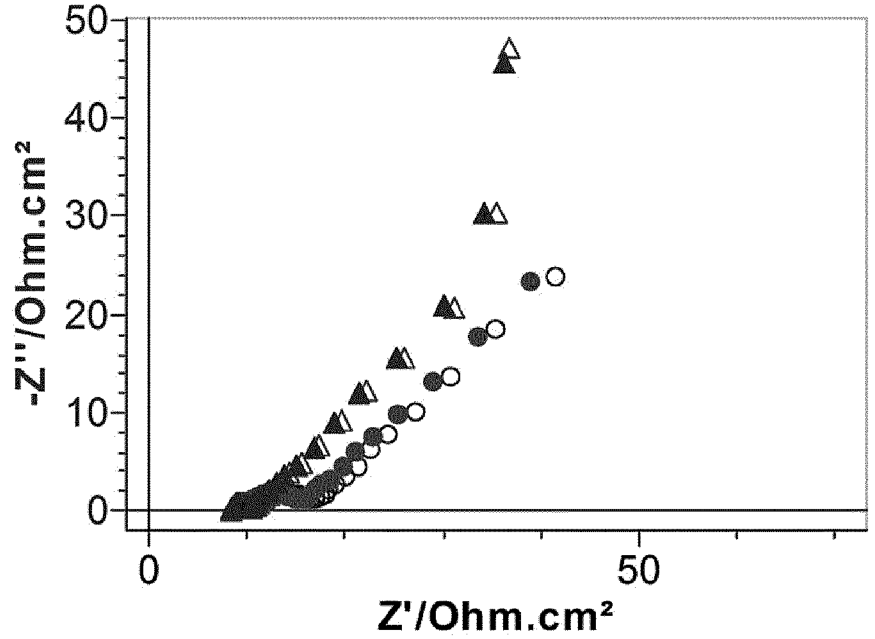

50
40
30
20
10
0
-Z''/Ohm.cm²
0
50
Z'/Ohm.cm²

Fig. 3a

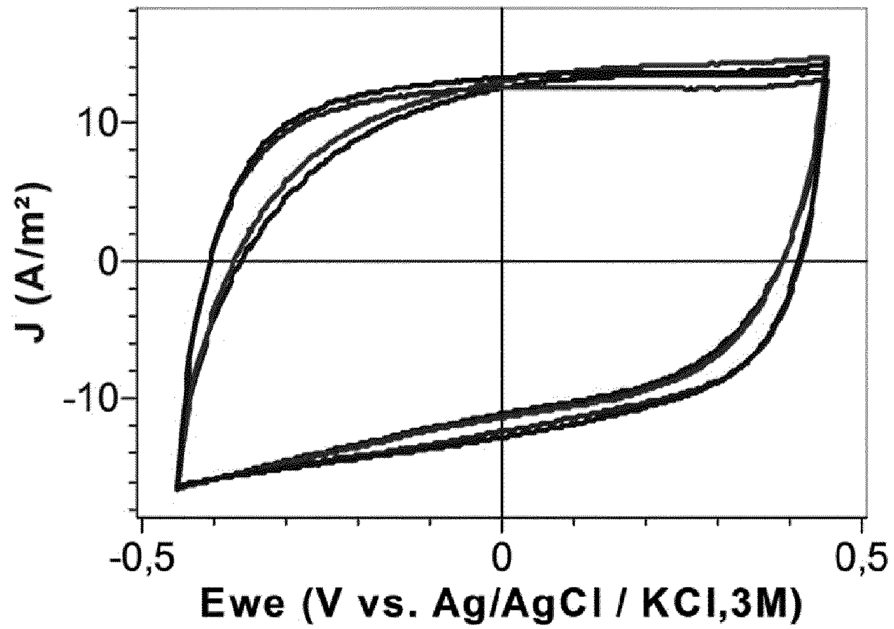

10
0
-10
J (A/m²)
-0,5
0
0,5
Ewe (V vs. Ag/AgCl / KCl,3M)

Fig. 3b

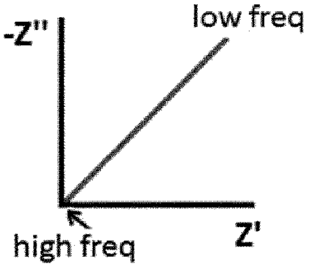


Fig. 3c

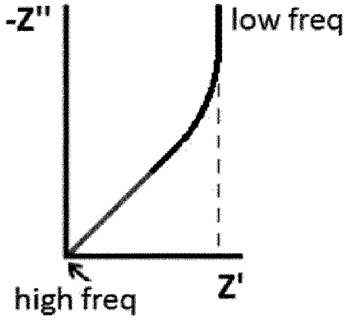


Fig. 3d

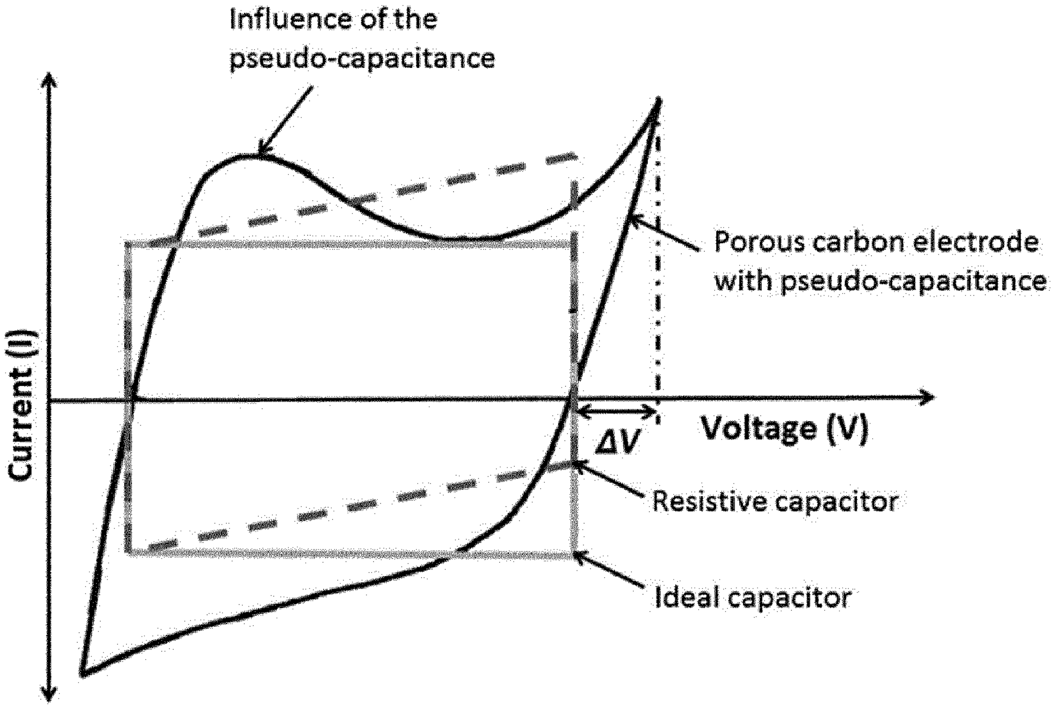


Fig. 3e

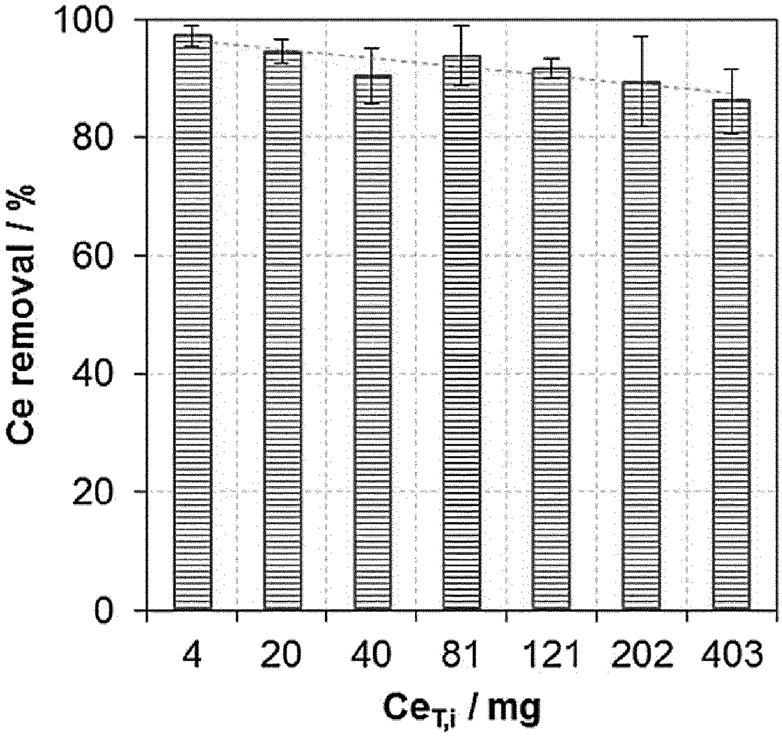

100
80
60
40
20
0
Ce removal / %
4
20
40
81
121
202
403
$Ce_{T,i}$ / mg

Fig. 4

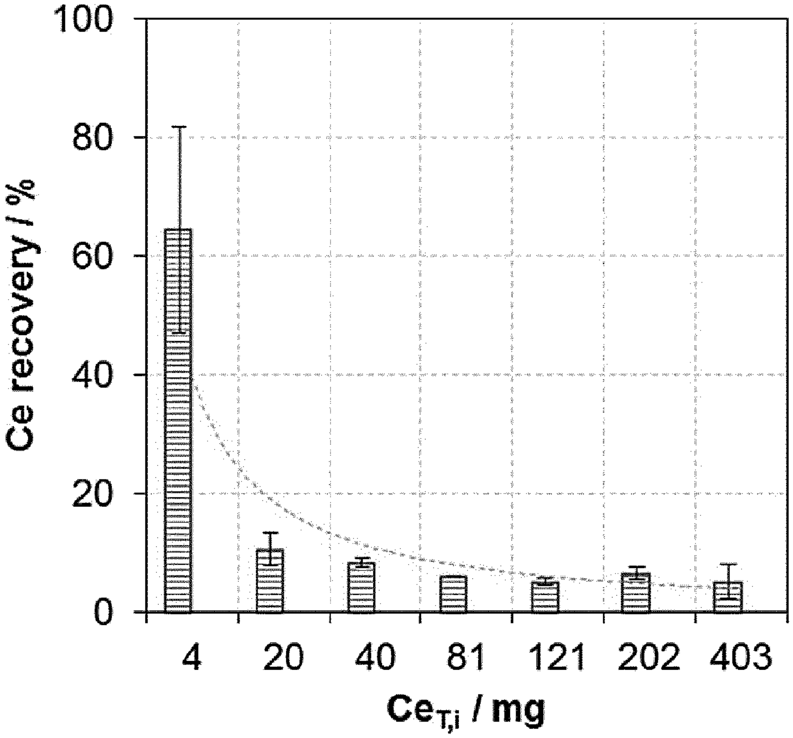

100
80
60
40
20
0
Ce recovery / %
4
20
40
81
121
202
403
$Ce_{T,i}$ / mg

Fig. 5

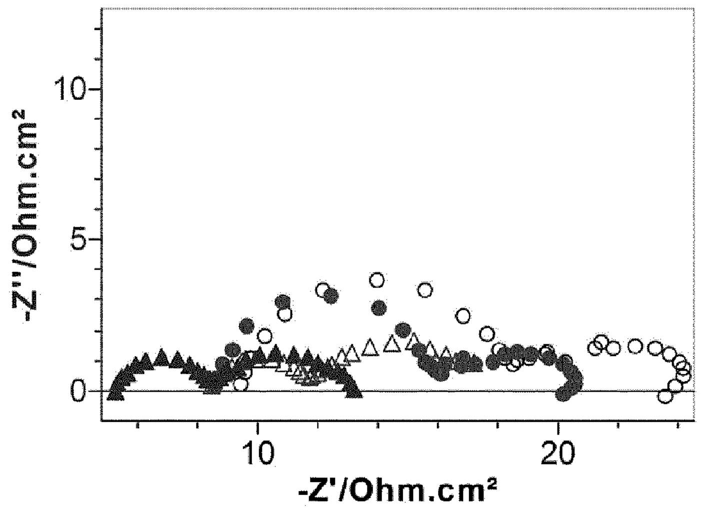


Fig. 6a

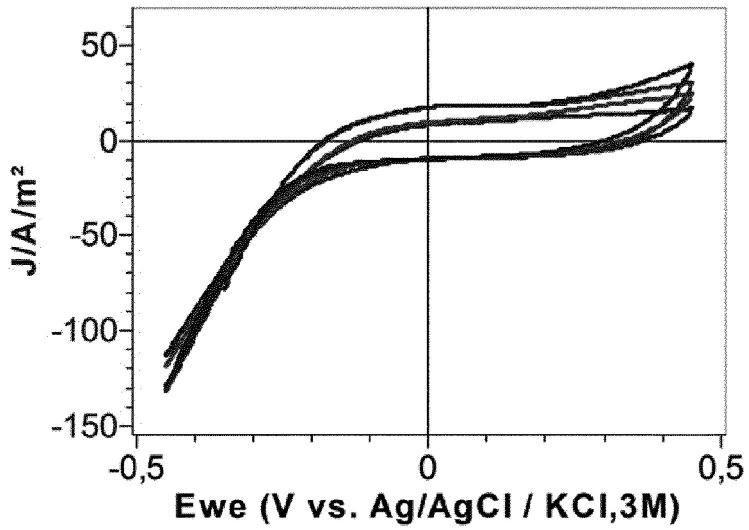


Fig. 6b

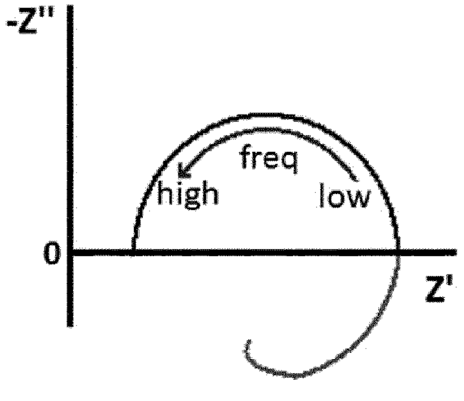
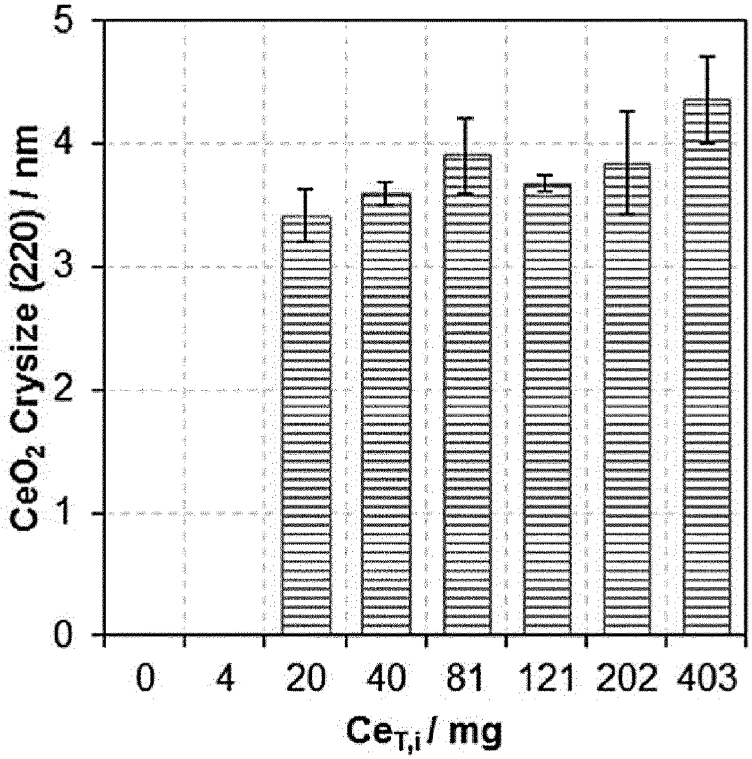
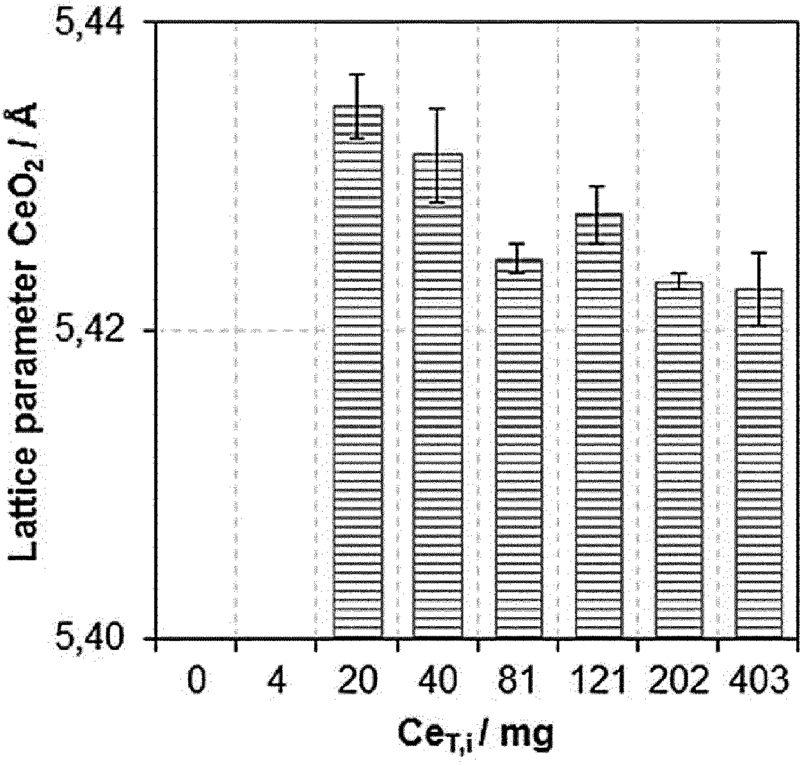


Fig. 6c



CeO₂ Crysize (220) / nm
5
4
3
2
1
0
0
4
20
40
81
121
202
403
Ce$_{T,i}$ / mg

Fig. 7a



Lattice parameter CeO₂ / Å
5,44
5,42
5,40
0
4
20
40
81
121
202
403
Ce$_{T,i}$ / mg

Fig. 7b

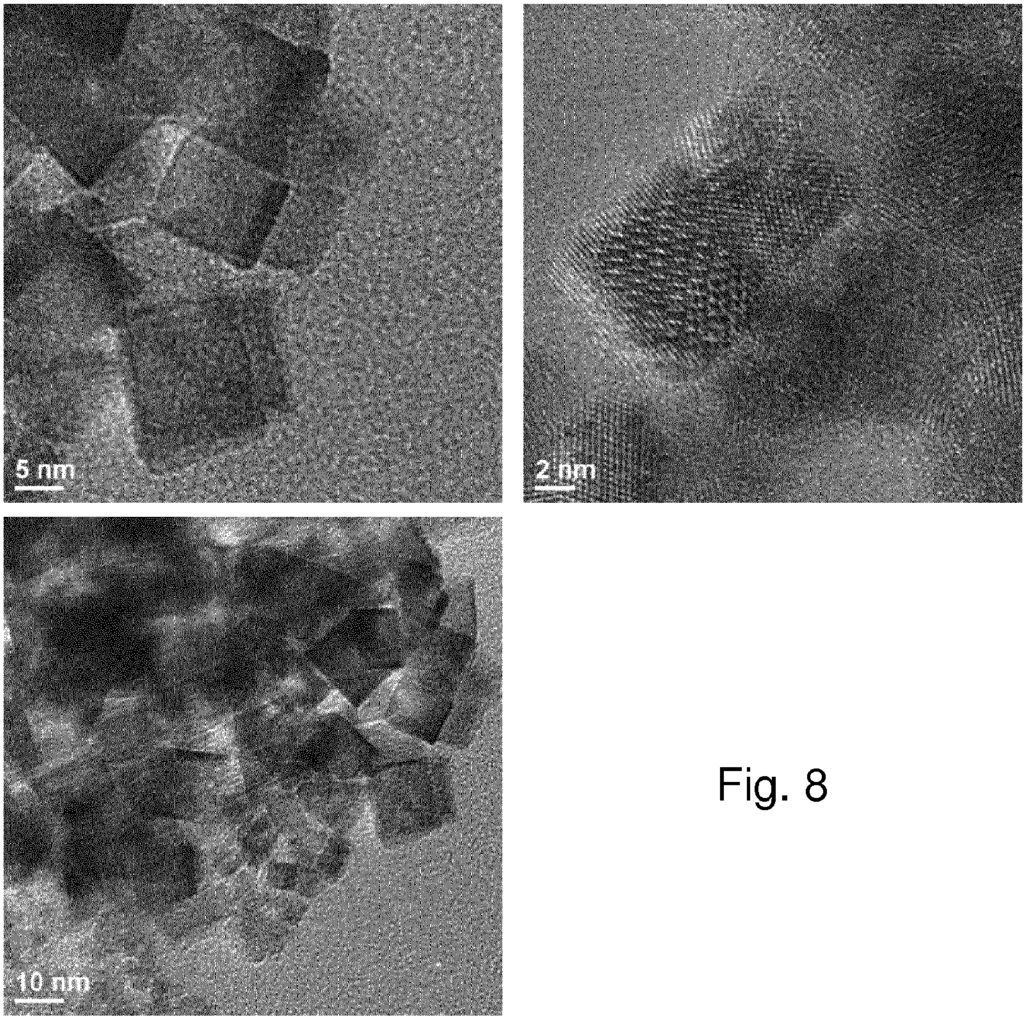


Fig. 8

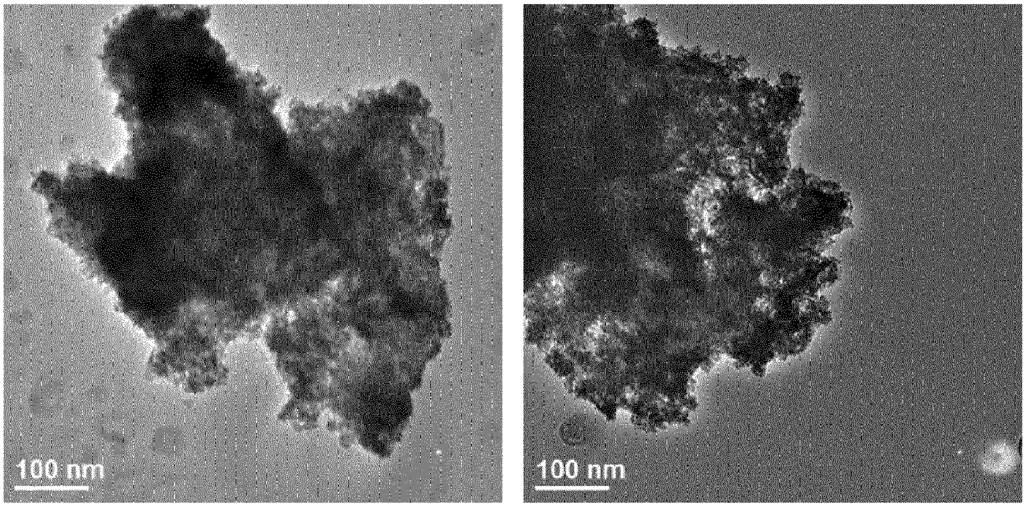


Fig. 9

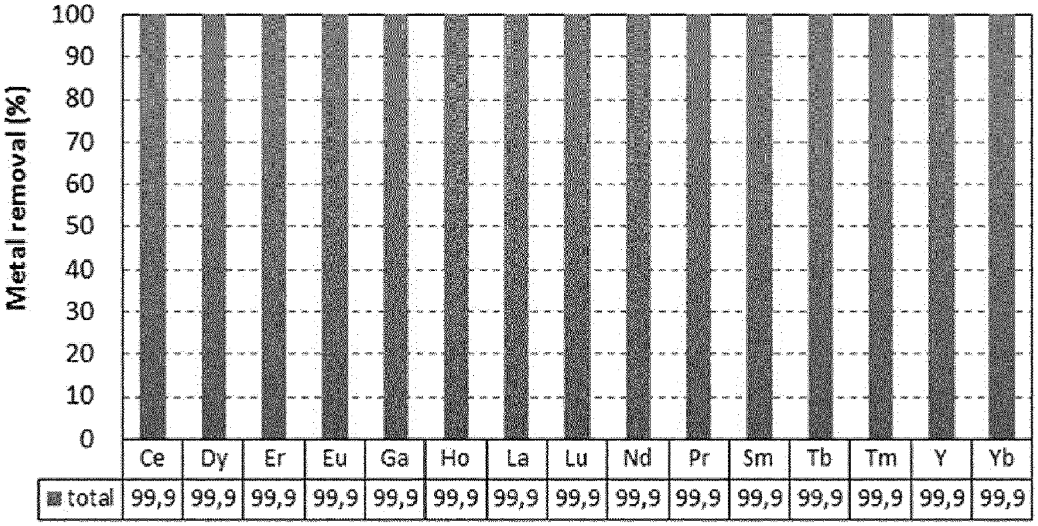

Metal removal (%)
100
90
80
70
60
50
40
30
20
10
0
Ce Dy Er Eu Ga Ho La Lu Nd Pr Sm Tb Tm Y Yb
▩ total 99,9 99,9 99,9 99,9 99,9 99,9 99,9 99,9 99,9 99,9 99,9 99,9 99,9 99,9 99,9

Fig. 10

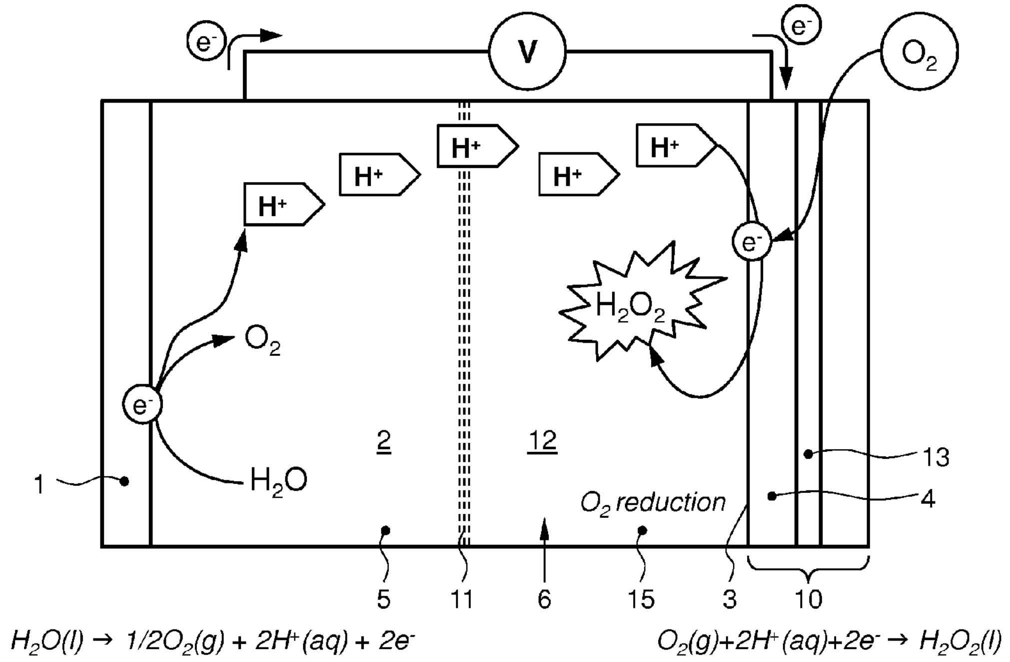

e-
V
e-
O2
H+
H+
H+
H+
H+
e-
H2O2
O2
e-
2
12
H2O
1
O2 reduction
13
4
5
11
6
15
3
10
H2O(l) → 1/2O2(g) + 2H+(aq) + 2e-
O2(g)+2H+(aq)+2e- → H2O2(l)

Fig. 11

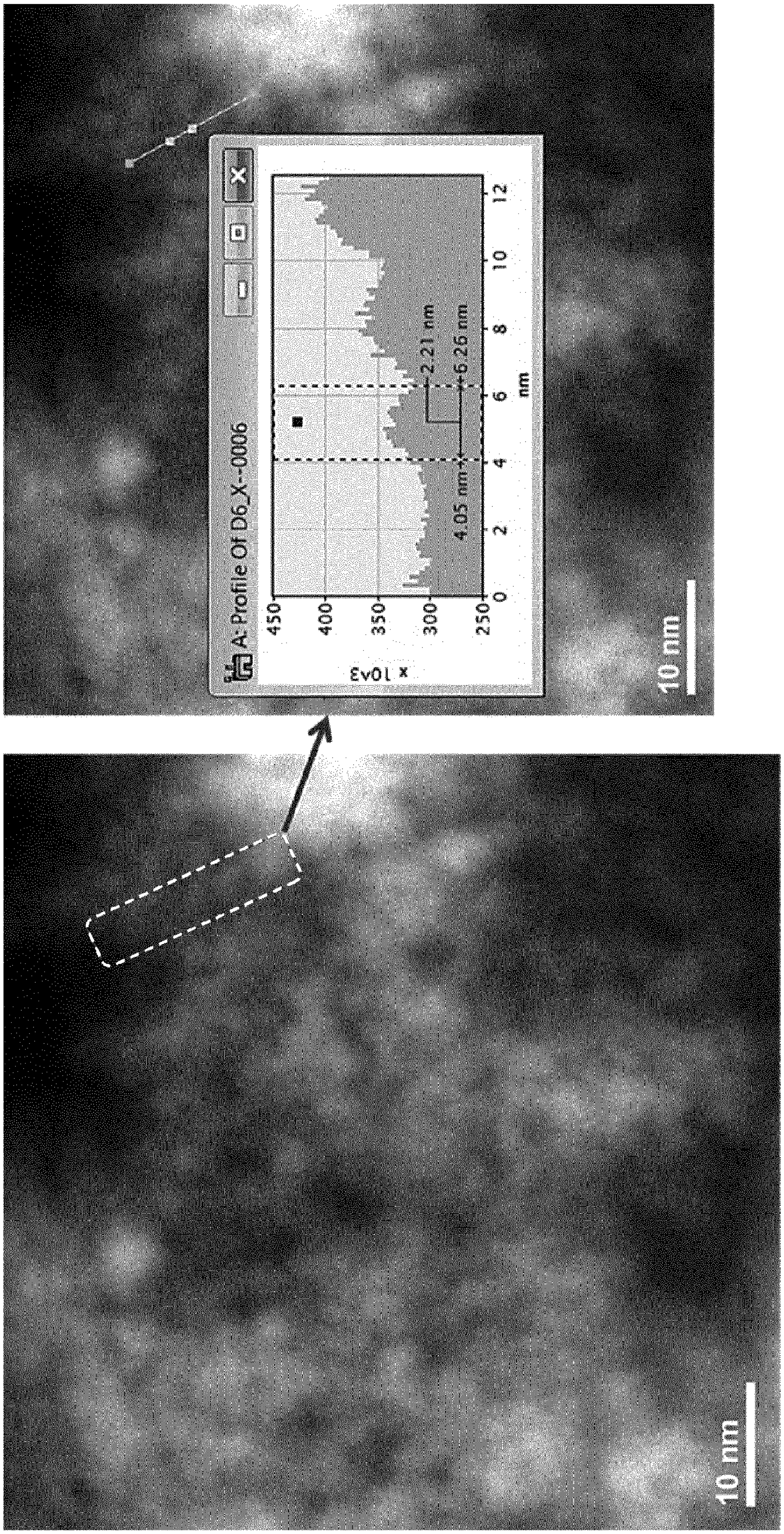

A:Profile Of D6_X--0006
x 10^3
450
400
350
300
250
0
2
4
6
8
10
12
nm
2.21 nm
4.05 nm
6.26 nm
10 nm
10 nm

Fig. 12

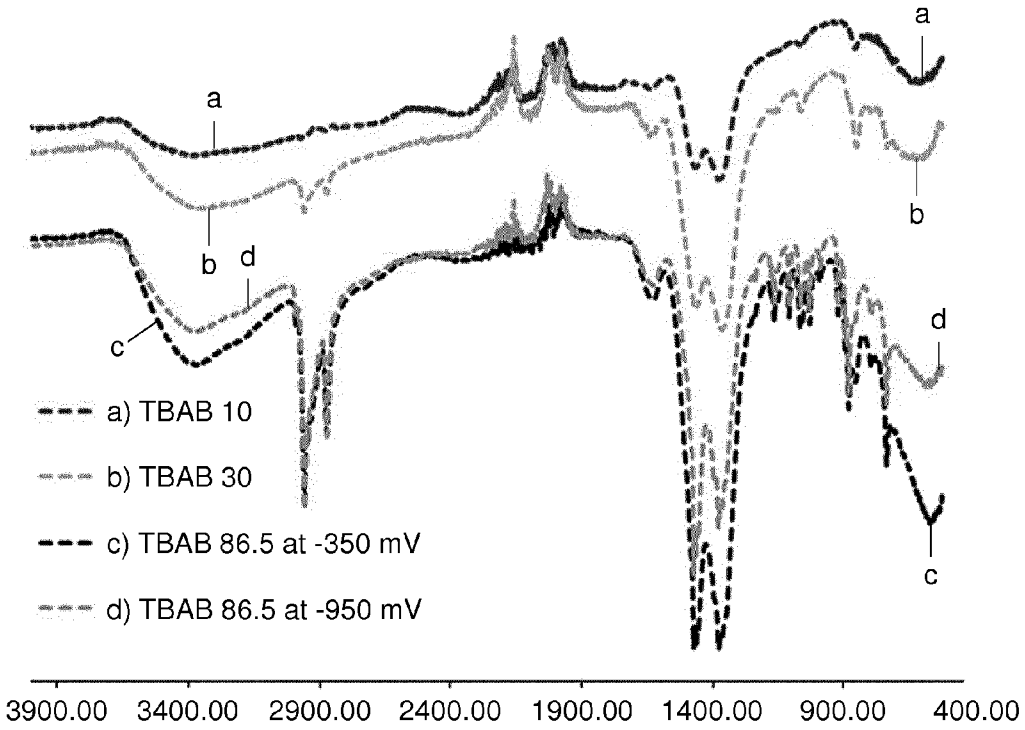

a
a
b
b
d
d
c
c
a) TBAB 10
b) TBAB 30
c) TBAB 86.5 at -350 mV
d) TBAB 86.5 at -950 mV
3900.00
3400.00
2900.00
2400.00
1900.00
1400.00
900.00
400.00

Fig. 13a

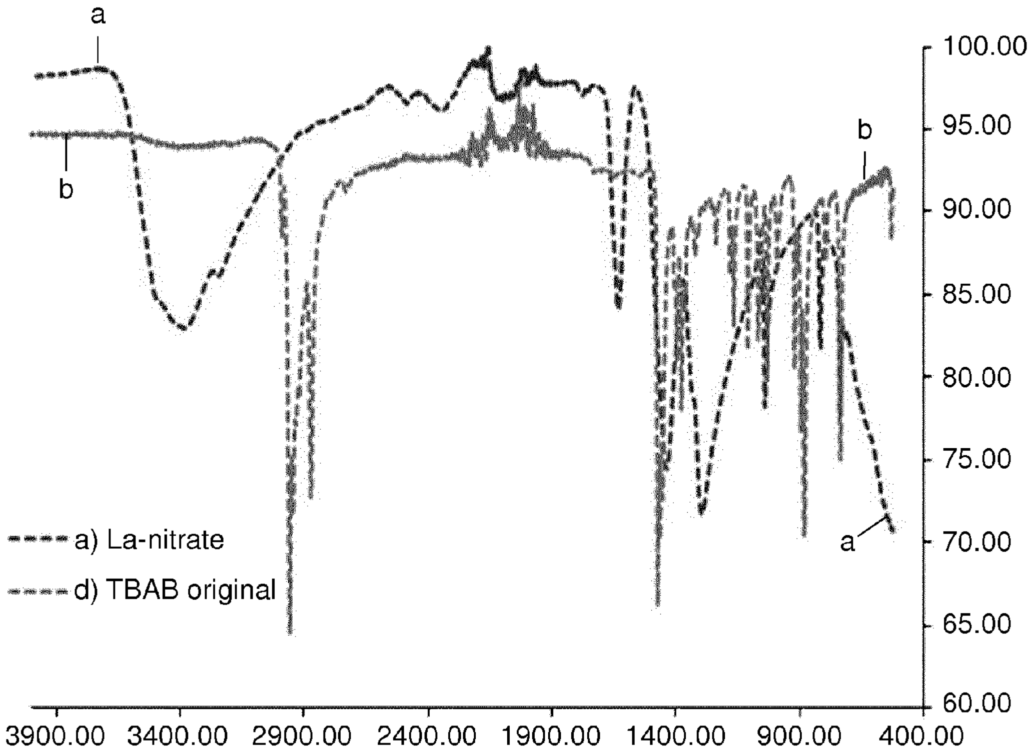

a
b
b
a
a) La-nitrate
d) TBAB original
100.00
95.00
90.00
85.00
80.00
75.00
70.00
65.00
60.00
3900.00
3400.00
2900.00
2400.00
1900.00
1400.00
900.00
400.00

Fig. 13b

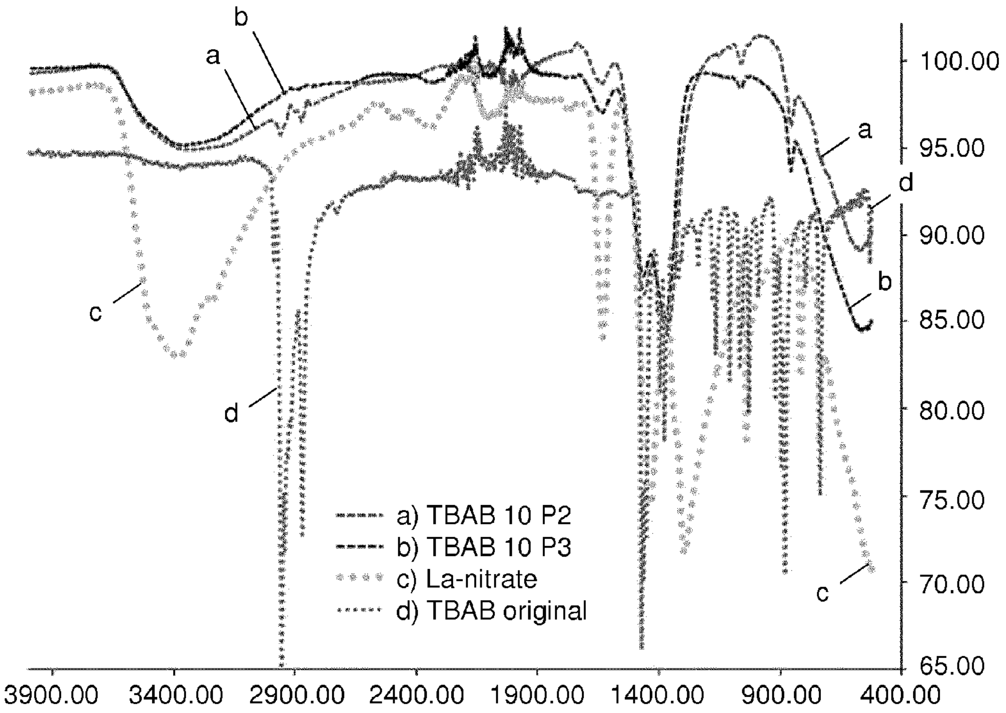

a
b
c
d
a
d
b
c
100.00
95.00
90.00
85.00
80.00
75.00
70.00
65.00
3900.00
3400.00
2900.00
2400.00
1900.00
1400.00
900.00
400.00
a) TBAB 10 P2
b) TBAB 10 P3
c) La-nitrate
d) TBAB original

Fig. 13c

Fig. 14

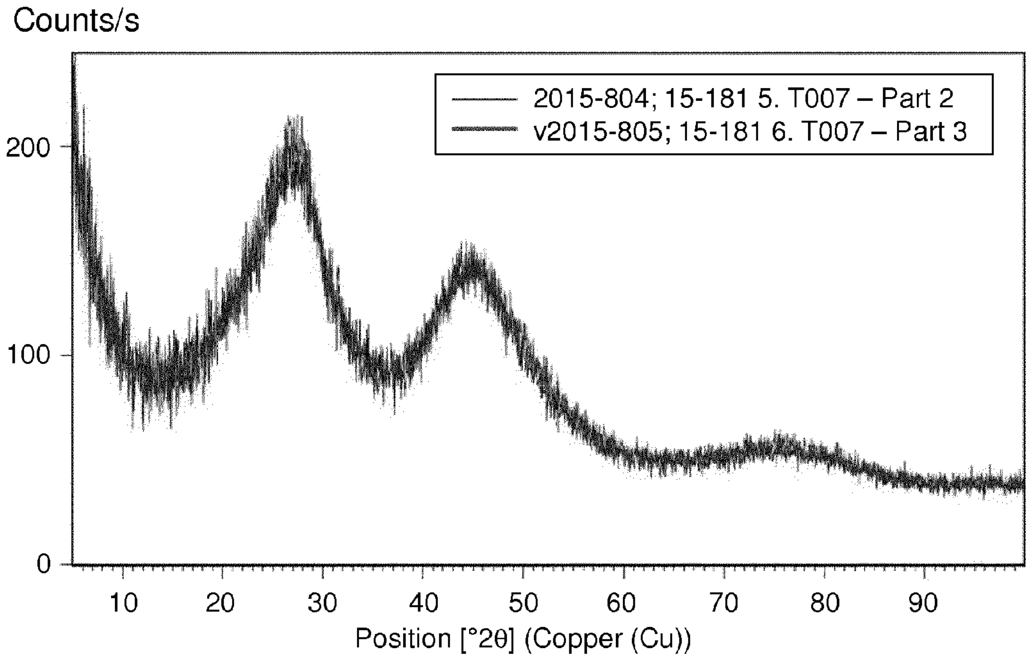

Counts/s
2015-804; 15-181 5. T007 – Part 2
v2015-805; 15-181 6. T007 – Part 3
200
100
0
10
20
30
40
50
60
70
80
90
Position [°2θ] (Copper (Cu))

Fig. 15

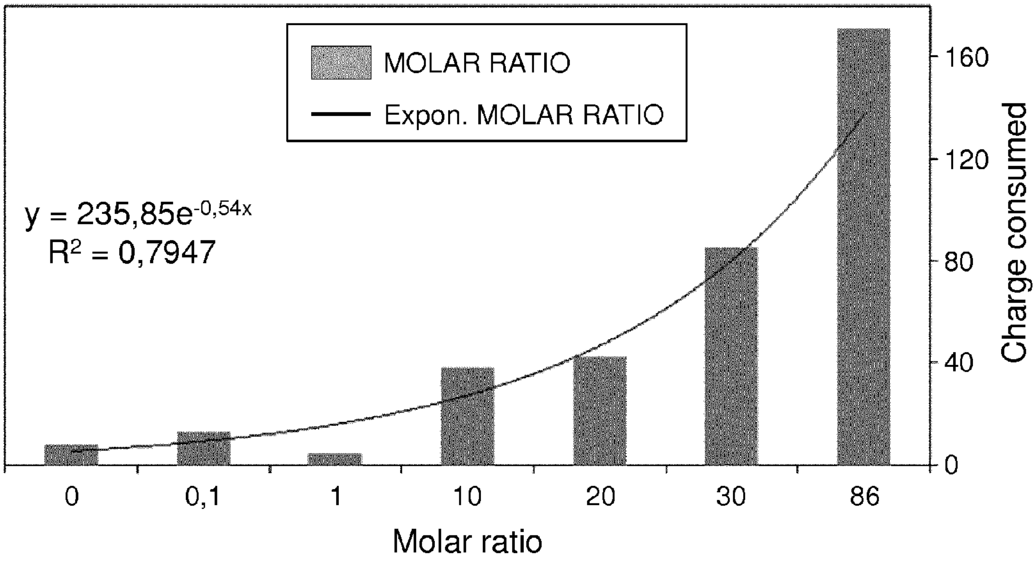

MOLAR RATIO
Expon. MOLAR RATIO
y = 235,85e-0,54x
R2 = 0,7947
160
120
80
40
0
Charge consumed
0
0,1
1
10
20
30
86
Molar ratio

Fig. 16

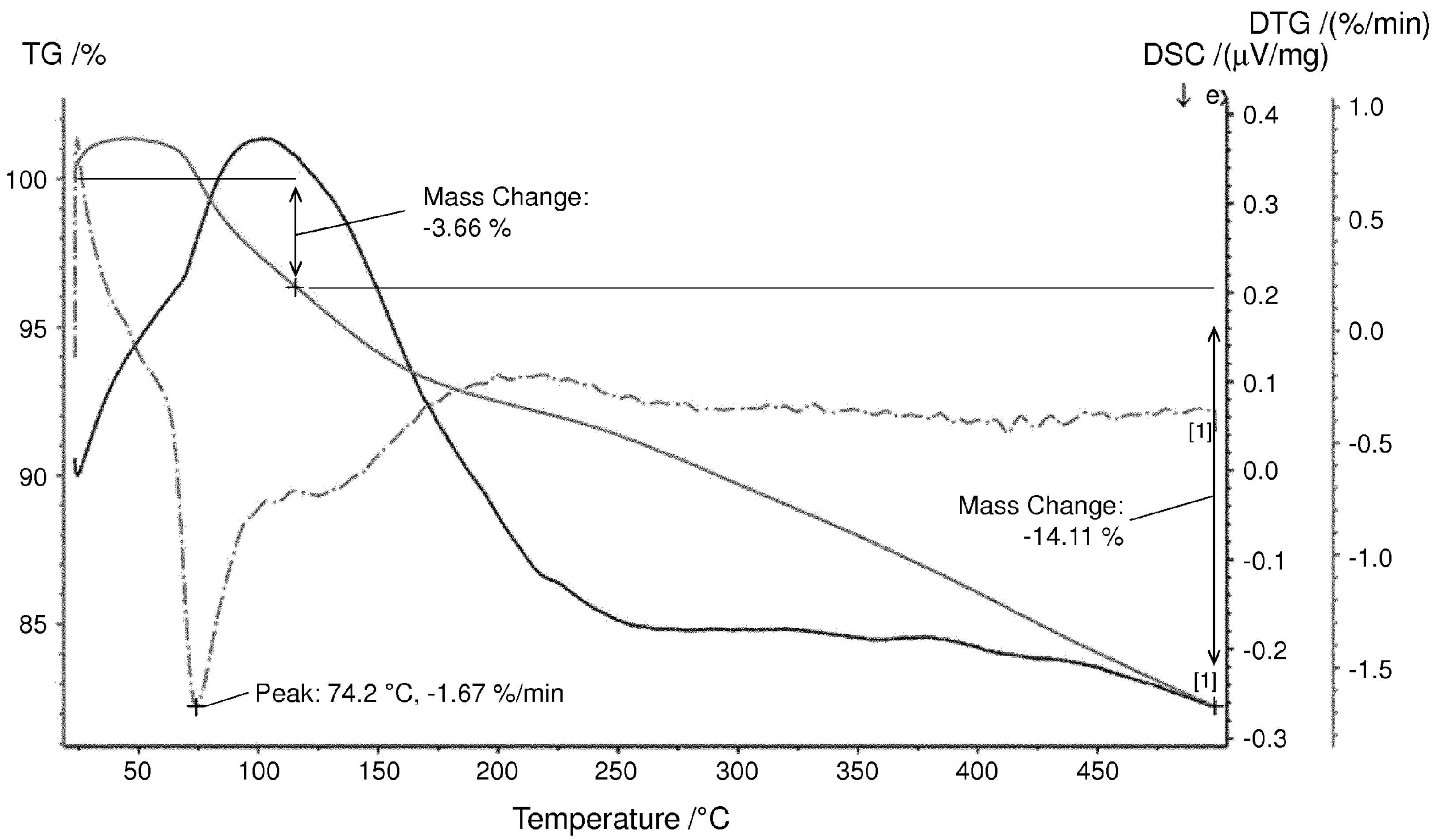

TG /%
DTG /(%/min)
DSC /(µV/mg)
↓ exo
100
95
90
85
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
1.0
0.5
0.0
-0.5
-1.0
-1.5
Mass Change:
-3.66 %
Mass Change:
-14.11 %
[1]
[1]
Peak: 74.2 °C, -1.67 %/min
50
100
150
200
250
300
350
400
450
Temperature /°C

Fig. 17

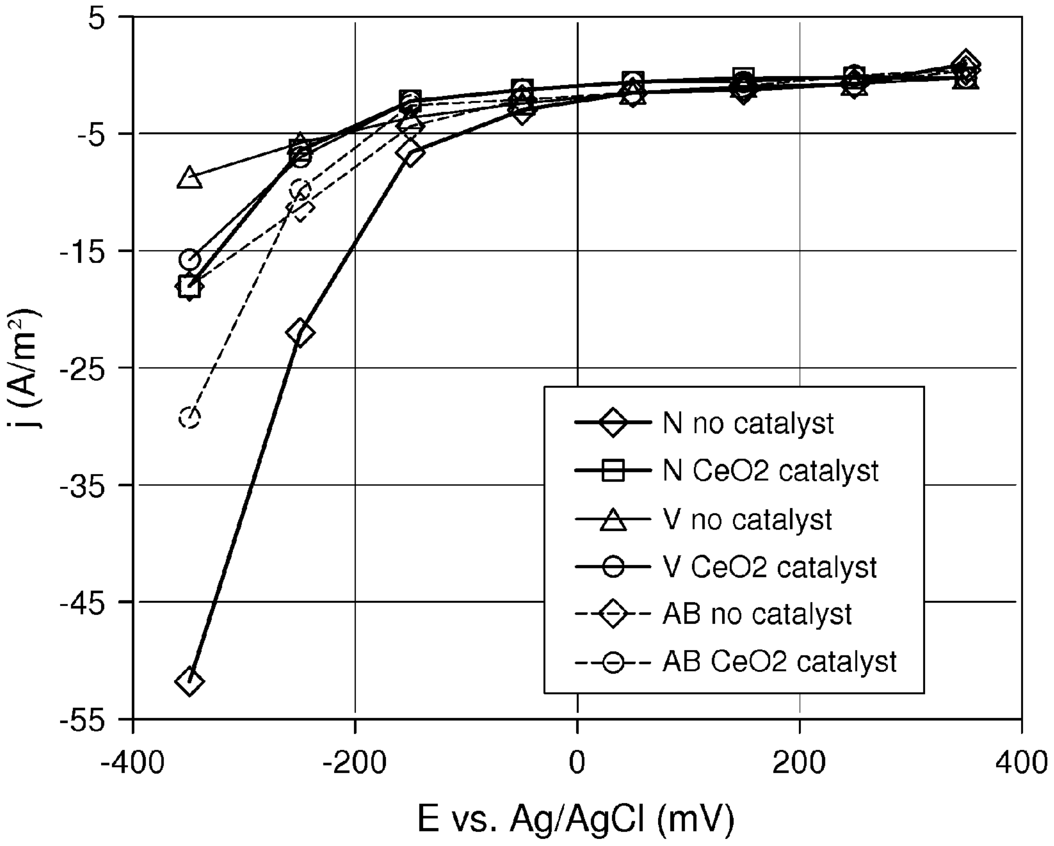

5
-5
-15
-25
-35
-45
-55
j (A/m²)
-400
-200
0
200
400
E vs. Ag/AgCl (mV)
N no catalyst
N CeO2 catalyst
V no catalyst
V CeO2 catalyst
AB no catalyst
AB CeO2 catalyst

Fig. 18

AN ELECTROCHEMICAL PROCESS FOR PREPARING A COMPOUND COMPRISING A METAL OR METALLOID AND A PEROXIDE, IONIC OR RADICAL SPECIES

[0001] The present invention relates to electrochemical process for recovering a metal element or a metalloid element or a mixture of two or more thereof from at least one water soluble precursor compound comprising the metal element or a metalloid element or two or more thereof, in the form of one or more nano particles of at least one reaction product, according to the preamble of the first claim.

[0002] The present invention further relates to nano particles, in particular nano crystals obtained with that process and to a device for carrying out the process of the invention.

BACKGROUND OF THE INVENTION

[0003] Nano particles and their composites exhibit unconventional electronic, optical, magnetic and chemical properties with respect to bulk phase particles and macroscopic crystals. Hence, they offer new or improved properties for application in a wide variety of fields ranging from catalysis, cosmetics, textiles, nano-electronics, high-tech components and defense gadgets, to pharmaceuticals, medical uses, sensors and diagnostics. At the smallest sizes (e.g. <20-50 nm), nano particle properties typically vary irregularly and are specific to each size (in Rao C. N. R., Thomas P. J., Kulkami G. U., Nano crystals: Synthesis, Properties and Applications). Regardless of the method used for their preparation many challenges have to be to overcome, like controlling particle growth, crystallinity, stability and reproducibility. A high quality synthesis procedure should desirably produce nano particles with a controlled size distribution, often a narrow size distribution is aimed at. The narrower the size distribution, the more attractive the synthesis procedure. The best synthesis procedures available today produce nano crystals with a size distribution of about 5%. Shape control is also an important feature. Synthesis methods that provide crystalline nano particles are preferred, as well as the methods that provide shape stabilization. Particularly preferred are synthesis methods that do not employ hazardous solvents, thinking of environmental sustainability.

[0004] Modern methods for synthesizing amorphous or crystalline nano particles may include chemical reaction steps, as well as physical treatment and biological steps. Chemical methods for producing crystalline nano particles offer the advantage over physical methods that milder reaction conditions may be used. In comparison with purely biological methods, an improved control may be achieved. Chemical methods typically employ the steps of crystal seeding, permitting particle growth to take place and terminating particle growth once the desired particle size has been obtained. Since these steps are often inseparable, synthesis is often initiated by providing a nano crystal precursor, a solvent and termination (capping) agents. Electrochemical synthesis is often employed for the production of zero-valent, metal nano crystals, by the steps of oxidative dissolution of an anode, migration of metal ions to the cathode and reduction to the zero valent state, nucleation followed by particle growth, addition of capping agents (typically quaternary ammonium salts containing long-chain alkanes) to inhibit growth, and precipitation of the nano crystals. The size of nano crystals may be tuned a.o. by altering current density, varying the distance between the electrodes, controlling the reaction time, temperature and the polarity of the solvent. Chemical and classical electrochemical methods typically result in the formation of nano crystals having an average particle size around 100 nm. In a few cases, formation of nanocrystals with an average particle size below 100 nm has been observed, however these exhibit highly polydisperse (non-uniform) size and shape distributions.

[0005] US20060068026 discloses a thermal electrochemical method for preparing a colloidal stable suspension of zero-valent naked metal or metal-alloy nano crystals. The method comprises the steps of at least partly immersing into essentially contaminant-free water, a metallic sacrificial anode that includes an essentially contaminant-free metal starting material for the nano crystals and a cathode; and applying a voltage potential across the anode and the cathode to form a colloidally stable suspension of naked metal nano crystals composed essentially of metal from the metallic sacrificial anode.

[0006] When analyzing existing methods for synthesizing nano particles, the inventors realized that the existing techniques can be regarded from a different perspective. The chemical precursors for the nano particles are usually present in a dissolved state in the solution that is to be treated, for example the chemical precursors are dissolved in an aqueous matrix. Formation of the nano particles and their conversion into a stable solid precipitate has the consequence that the water soluble ions are removed from the aqueous matrix. The method for synthesizing nano particles can therefore also be regarded as a method for removing water soluble compounds from a solution and recovering them for example as a solid precipitate.

[0007] This is of special interest in the field of recovery of critical raw mineral materials, especially those with high technological interest such as the rare earth elements (REE) which are used in the manufacturing of electronic and telecommunication devices and high-tech applications, strategic and clean energy technologies and defense instruments to name a few examples. The REE are ranked as critical raw materials not only due to their wide applicability, but primarily due to the risk of supply interruption and probably also due to their high economic value. A key measure to anticipate REE supply vulnerabilities is recycling from end-of-life products; yet recycling possibilities are far from sufficient to meet the REE demand. As the risk of supply interruption and the value of REE rise, other matrices not yet prospected start to make economic sense for recovery.

[0008] WO 2012115273 A1 discloses a method for the extraction and separation of lanthanoid and actinoid elements by contacting a solution of these elements with a nanostructure carrying a metal-adsorbent compound, capable of functioning as an adsorbent for the target metal. To recover the target metal, the adsorbent compound with the metal adsorbed to it is contacted with a back-extraction solution.

[0009] Another method for removing ionic species from fluids, for example impaired water supplies, which makes use of capacitive deionization is disclosed in US2011042219. The method disclosed in US2011042219 employs an electrodialysis and/or an electrodialysis reversal system that utilizes high-surface area, porous, non-Faraday electrodes—which they do not carry out electron transfer reactions. The system contains a membrane stack which includes alternating cation-transfer membranes and anion-transfer membranes, as well as a porous cathode and a porous anode. As direct current power is passed through the electrodes, cations and anions migrate to opposing electrodes, thereby causing a separation of the saline water into concentrate and dilute stream lines. A double layer capacitor with a high apparent capacitance may be thus formed on each electrode. The method is typically applicable in industries in which liquids may require ionic species removal including water, pharmaceuticals and food and beverage industries.

[0010] However, the above described methods do not provide true, economically feasible recovery rates, where possible in a form which permits re-use of the metal. The existing extraction methods for extracting REE or other critical metals from aqueous matrixes, e.g. to meet regulatory requirements, are insufficient and need to be adapted to provide a commercially interesting product.

[0011] US2015/0200082 A1 discloses a method of manufacturing particles of metal hydroxides, such as indium, tin, copper, gallium, zinc, aluminum, iron, nickel, manganese, and lithium, or an alloy containing at least one type selected from these metals, wherein the metal particles have a uniform particle diameter of 100 nm. A gas diffusion electrode is submerged in an electrolyte, for example ammonium nitrate, the anode is defined by the metal or the conductive metal oxide. Oxygen supplied to the cathode is reduced at the gas-liquid interface, thereby generating hydroxide ions ($O_2+2H_2O+4e^-\rightarrow 4OH^-$), causing the pH to increase as the process continues. The standard electrode potential (+0.40 V) of the reduction reaction of the oxygen being higher than the standard electrode potential (+0.01 V) of the reduction reaction of the nitrate ion, reduction of the nitrate ions rarely occurs. Metal ions eluted from the anode during electrolysis react with the hydroxide ions in the electrolytic solution to form metal hydroxide particles. The alkaline conditions in which the reaction is carried out cause particle diameters to increase, and obtaining the metal hydroxides as particles with a uniform desired particle diameter is hard to achieve. If so desired, pH and temperature of the electrolyte can be stabilized. When analysing the morphology of the particles, it appeared that each particle consists of a plurality of smaller particles aggregated to form a larger particle.

[0012] U.S. Pat. No. 3,073,763 discloses a method for the electrolytic production of iron oxides or mixtures of metal oxides which predominantly contain iron oxide, using an iron anode and one or more other metal anodes and a cathode consisting of a conductive material, e.g. metal or carbon. An alkaline salt solution, the anions of which do not form insoluble salts with the metals of the anodes and have a greater affinity to hydrogen than to iron is used as the electrolyte. In the course of the process, the metals at the anode will dissolve and contact the alkaline medium which has formed adjacent the cathode. If oxygen is supplied, the metal ions are converted in the electrolyte solution into the corresponding oxides, which precipitate in solution as particles having a large average particle size in the order of 100 nm or more. In the process of U.S. Pat. No. 3,073,763 no reduction of oxygen takes place.

[0013] U.S. Pat. No. 4,067,788 discloses a method for producing finely divided metal powders, in particular powders of nickel, silver, gold and the platinum group metals, having particles ranging in size from about 0.5 micron to about 10 micron. The anode is made of the metal to be finely divided as the oxide, the hydroxide or the metal itself. The anode is immersed in an alkaline solution of a salt, having a typical pH of between 8 and 12, the anion of the salt being soluble when combined with said metal. The cathode is a catalyzed air electrode. Since the metal ions produced at the surface of anode do not immediately react with the hydroxyl ions of the solution, and since the insoluble oxides or hydroxides are formed in solution at a perceptible distance from the surface of the anode, the particle size may be controlled by recirculation of the electrolyte. In order to further increase the particle size of the oxide or hydroxide, a portion of the solid material is returned to the cell in which the process is carried out to serve as nuclei on which additional oxide or hydroxide is deposited. The final step in the process is the chemical reduction of the metal oxide or metal hydroxide to the finely divided metal, for example using formaldehyde or inverted sugar.

[0014] U.S. Pat. No. 6,235,185 discloses a method and an apparatus for producing particles of a metal compound such as a metal oxide or a metal hydroxide having particle diameters of not greater than 1 micron, in particular 1 to 1000 nm, preferably 5 to 100 nm, The term "particle diameter" herein means the volume average particle diameter of 200 or more particles observed by means of a transmission electron microscope and a sharp particle size distribution, starting from a less expensive starting material and using a simplified production facility. Thereto an electrolytic solution which contains metal ions as a starting material for the ultrafine metal compound particles is provided in the anode chamber, an alkaline electrolytic solution is provided in the cathode chamber. A voltage is applied between the anode and the cathode, to induce transfer of the metal ions from the anodic side chamber to the cathodic side chamber through an ion exchange layer. Ultrafine metal compound particles are precipitated in the alkaline electrolytic solution in the cathode chamber. Examples of metals suitable for use with the method of U.S. Pat. No. 6,235,185 include lithium, magnesium, aluminum, calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, germanium, rubidium, strontium, yttrium, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, cadmium, indium, tin, antimony, tellurium, cesium, barium, tantalum, tungsten, osmium, platinum, gold, mercury, lead, bismuth, cerium, neodymium, samarium and europium, or combinations hereof.

[0015] US2004/0108220 A1 discloses a process for the production of amorphous and/or crystalline mixed oxides of metals with mean particle diameters ranging from 1 to 500 nm, more particularly metals of the third to fifth main group or the secondary groups of the periodic system. Ions dissolved in an organic electrolyte of those metals of which the (mixed) oxide is to be produced in the electrolyte of the cathode compartment, are electrochemically reduced at the cathode in the presence of air as an oxidizing agent. The cathode compartment is separated from the anode compartment by a porous partition diaphragm which is permeable to cations and anions, but prevents the passage of elemental halogen from the anode to the cathode compartment. Preferred organic electrolytes include alcohols, polyalcohols or mixtures and derivatives thereof, ketones, ethers, nitrites, organic carbonates and aromatic compounds, tetrahydrofuran, acetone, acetonitrile, toluene. The organic electrolyte may contain small quantities of water, for example from about 0.01 to about 2% by weight. Air introduced in the form of small bubbles on the one hand, provides for a fine distribution of the oxidizing agent in the cathode compartment and on the other hand counteracts formation of solid metal oxide on the cathode by providing a constant mixing of the electrolyte, and instead ensures that the metal oxide particles are flushed from the cathode and dispersed in the electrolyte.

[0016] Although US2004/0108220 A1 is said to produce particles of amorphous and/or crystalline mixed oxides of metals with mean particle diameters ranging from 1 to 500 nm, the examples do not reveal the actual particle size obtained. Moreover, the process involves the use of an organic electrolyte and is therefore not suitable for example for recovering metal ions from aqueous solutions.

[0017] A need remains for an economically feasible electrochemical process which permits to recover from a water soluble precursor compound containing a metal or metalloid element or two or more thereof, a reaction product containing the metal or metalloid element or two or more thereof. A particular need remains for an economically feasible process which permits to recover such metal or metalloid elements in the form of crystalline nano particles of a compound or a mixture of two or more compounds containing the at least one metal or metalloid element, wherein the crystalline nano particles have an average particle diameter of 50 nm or smaller, preferably 30 nm or smaller, more preferably 20 nm or smaller, most preferably 10 nm or smaller or even 5 nm or smaller. More particularly, a need remains for an electrochemical process which permits to produce such crystalline particles with a controlled particle size distribution, preferably a narrow particle size distribution or a so-called monodisperse particle size distribution. This process should be suitable for recovering the commonly used metal or metalloid elements as well as those which are less commonly used.

[0018] The present invention therefore aims at providing an economically feasible method for isolating from at least one water soluble precursor compound comprising a metal or a metalloid element or two or more thereof, nano particles, in particular crystalline nano particles, of at least one reaction product comprising a metal or a metalloid element or two or more thereof.

[0019] This is achieved by the present invention with a method which shows the technical features of the characterizing portion of the first claim.

[0020] Thereto the electrochemical process of this invention comprises the steps of

- **[0021]** supplying the water soluble precursor compound to a water-based catholyte of a cathode compartment of an electrochemical cell, equipped with a cathode comprising a gas diffusion electrode, wherein the gas diffusion electrode comprises a porous electrochemically active material having a BET surface area of at least 50 m^2/g,
- **[0022]** adjusting the pH of the catholyte to a pH which is smaller than the pKa of the water soluble precursor compound,
- **[0023]** supplying at least one oxidant gas to the gas diffusion electrode,
- **[0024]** subjecting the cathode to an electrochemical potential to cause reduction of the at least one oxidant gas to one or more of the corresponding peroxide, ionic and/or radical reactive species capable of reacting with a cation comprising the metal element, or the metalloid element or a mixture of two or more thereof, to form at least one nano particle, in particular at least one nano crystal, of the at least one reaction product with an average particle size, in particular an average crystallite size equal to or smaller than 30.0 nm.

[0025] The inventors have observed that subjecting the cathode to an electrochemical potential which is chosen such that it is capable of causing reduction of an oxidant gas supplied to it, permits to induce at the electrochemically active surface of the gas diffusion electrode of the cathode, in other words at the electrochemically active surface of the cathode, a redox transformation. This redox transformation involves on the one hand a reduction of the oxidant gas, and on the other hand an in situ oxidation of the metal and/or metalloid element contained in the water soluble precursor compound, to a higher oxidation state. This is surprising, as the skilled person would typically expect a reduction reaction of the metal and/or metalloid element to occur at the cathode. The assumption that an in situ oxidation of the at least one metal and/or metalloid element takes place is supported by the observation that the conductivity of the catholyte decreases with an increasing degree of recovery of metal or metalloid ion from the aqueous solution, i.e. an increasing formation of nano particles, in particular nano crystals of the reaction product. The inventors have also observed that the oxidized at least one metal and/or metalloid element having a positive valence adsorb at least temporarily to the electrochemically active surface of the cathode, and thereby form an interface with the catholyte.

[0026] The electrochemical potential or range of electrochemical potentials at which reduction of the oxidant gas may occur, is well known to the skilled person and is represented by the Nernst equation. The Nernst equation is an equation that relates the reduction potential of a half-cell or the total voltage at any point in time to the standard electrode potential, temperature, activity and reaction quotient of the underlying reactions and species used. The Nernst equation may be written as follows:

$$E = E^0 + \frac{RT}{zF}\ln\frac{a_{Ox}}{a_{Red}} \text{ or } E = E^0 + \frac{RT}{zF}\ln Q$$

where

- **[0027]** E is the half-cell reduction potential at the temperature of interest
- **[0028]** E^0 is the standard half-cell reduction potential
- **[0029]** R is the universal gas constant, R=8.314 472(15) $J\ K^{-1}\ mol^{-1}$
- **[0030]** T is the absolute temperature
- **[0031]** a is the chemical activity for the relevant species, where a_{Red} is the reducing agent and a_{Ox} is the oxidizing agent. $a_X=\gamma_X c_X$, where γ_X is the activity coefficient of species X. (Since activity coefficients tend to unity at low concentrations, activities in the Nernst equation are frequently replaced by simple concentrations.)
- **[0032]** F is the Faraday constant, the number of coulombs per mole of electrons: F=9.648 533 99(24)×10^4 C mol^{-1}
- **[0033]** z is the number of moles of electrons transferred in the cell reaction or half reaction
- **[0034]** Q_r is the reaction quotient.

At room temperature (25° C.), RT/F may be treated like a constant and replaced by 25.693 mV for cells.

[0035] The Nernst equation is frequently expressed in terms of base 10 logarithms (i.e. common logarithms) rather than natural logarithms, in which case it is written as follows for a cell at 25° C.:

$$E = E^0 + \frac{0.059}{z}\log_{10}\frac{a_{Ox}}{a_{Red}}$$

This equation can also be written as a function of pH, as follows:

$$E = E^0 + \frac{0.059}{z}\log_{10}\frac{a_{Ox}}{a_{Red}} - 0.059\frac{m}{z}\text{pH}$$

Where m represents the stoichiometric coefficient as per the reaction below:

$$a\text{A}+m\text{H}+ze^- \rightleftarrows b\text{B}+c\text{H}_2\text{O}$$

(see Pourbaix M (1976) Atlas of Electrochemical Equilibria in Aqueous Solutions. NACE Cebelcor. Houston, Tex.

[0036] The inventors believe that the redox transformation takes place at the active surface of the electrochemically active layer of the gas diffusion electrode, i.e. the external surface of the porous material forming the electrochemically active layer, as well as at the internal surface of the electrochemically active material or in other words on the active surface within the interior of pores of the porous electrochemically active material. The fact that the process also occurs within the pores of the electrochemically active material has been observed when the electric polarization is stopped, by the release of the majority of the nano particles, in particular nano crystals into the electrolyte when stopping the electric polarization.

[0037] Without wanting to be bound by this theory, the inventors assume that the reduction of the oxidant gas at the cathode may give rise to the formation of one or more peroxide, ionic and/or radical species, usually polyatomic species, which are adsorbed to the electrochemically active surface of the cathode and create there a local environment confined within the pores of the electrochemically active material. Within the pores of the electrochemically active material, a characteristic pH and redox potential may develop, which are different from that of both the solution and the external electrode surface. Supersaturation of the local environment with such species may occur.

[0038] The inventors further believe that the at least one water soluble precursor compound is dissolved in the electrolyte, in particular in the catholyte, in an at least partly dissociated state:

$$\text{MA} \leftrightarrow \text{M}^+ + \text{A}^-$$

with M^+ representing a cation of the metal element or metalloid element or a compound having a positive valence comprising the at least one metal element or metalloid element, or a mixture of two or more of the afore mentioned species. It is remarked that the at least one metal or metalloid ion or compound comprising the at least one metal element or metalloid element may have a positive valence of +1, +2, +3 or any other valence that may form for that species. The cations of the dissolve water soluble precursor compound contained in the aqueous electrolyte may migrate or diffuse from the electrolyte solution towards the cathode, adhere or be adsorbed to the external surface of the electrochemically active material and be adsorbed within the pores of the electrochemically active material, in particular to the active sites thereof. Adhesion of the positively charged cations to the electrochemically active surface of the gas diffusion electrode may take place through various mechanisms, and may involve adsorption forces, mainly Van der Waals forces. Besides that, an electric double layer may be formed at the active surface involving the cations, thus allowing for electrostatic adsorption or capacitive adsorption at the double layer, but reversible ion exchange adsorption, complexating or chelation and any other forms of adhesion or adsorption may take place as well.

[0039] The inventors further believe that at least part of the functional groups present on the surface of the electrochemically active material will be present in an at least partially dissociated state ($C^*—R^-$), especially when an electrochemical potential is applied to the electrode. These dissociated sites $C^*—R^-$ carrying an electric charge, may form ion exchange sites for the positively charged metal or metalloid ion. The surface of the electrochemically active layer may for example comprise weak protonic acid sites in the form ($C^*—RH$), which may dissociate into $C^*—R^-$ and H^+, where C^* represents an active site on the electrochemically active layer of the cathode.

[0040] In the presence of an oxidant gas such as oxygen or any other oxidant gas, the availability of the active sites in a dissociated state on the electrochemically active surface may be accelerated and a local environment may be created with extreme pH and redox conditions, which are different from those found in the bulk of the electrolyte solution and on the bare electrode surface:

$$\text{C}^*—\text{R}^-+\text{O}^2{}_{(g)}+e^-\rightarrow\text{C}^*—\text{RO}_{2ad}{}^{\cdot-}$$

$$\text{C}^*—\text{RO}_{2ad}{}^{\cdot-}+\text{H}_2\text{O}+e^-\rightarrow\text{C}^*—\text{RO}_{2ad}.\text{H}_{ad}+\text{OH}$$

$$\text{C}^*—\text{RO}_{2ad}.\text{H}_{ad}+e^-\rightarrow\text{C}^*—\text{R}^-+\text{HO}_2{}^-{}_{aq}$$

[0041] One or more positively charged ions, i.e. metal or metalloid ions or a compound comprising one or more of the metal or metalloid element, may be then adsorbed either directly to a $C^*—R^-$ site or to a reduced species of the oxidant gas, for example a peroxide radical, an ionic or other radical species, the peroxide radical being the most active species. Thereby a (polymetal ion polyoxy radical) or a (polymetalloid ion polyoxy radical) may be formed, which once adsorbed to an electrochemically active site and supersaturating such site may on the surface of the electrochemically active material of the cathode, act as a nucleation site for the formation of an oxidized compound comprising the at least one metal and/or at least one metalloid ion.

[0042] For example, in the case of the cerium ion (Ce^{3+}), this may lead to the following reactions:

$$\text{C}^*—\text{RO}_{2ad}{}^{\cdot-}+2\text{Ce}^{3+}+2e^-\rightarrow\text{C}^*—\text{RO}_{2ad}2\text{Ce}_{ad}$$

$$\text{C}^*—\text{RO}_{2ad}2\text{Ce}_{ad}+2\text{O}_{2(g)}+2e^-\rightarrow\text{C}^*—\text{RO}_{2ad}2\text{Ce}_{ad}2\text{O}_{2ad}{}^{\cdot}$$

$$\text{C}^*—\text{RO}_{2ad}2\text{Ce}_{ad}2\text{O}2_{ad}{}^{\cdot}+\text{H}_2\text{O}+\text{H}^++2e^-\rightarrow\text{C}^*—\text{RO}_{2ad}2\text{Ce}_{ad}2\text{O}_{2ad}2\text{H}_{ad}+\text{OH}^-$$

[0043] The electrochemically active surface of the gas diffusion electrode and the cathode includes the external surface as well as the active surface present in the pores of the electrochemically active material. In conventional gas diffusion electrodes which make use of a porous electrochemically active material, in particular a carbon based porous electrochemically active material, the active surface present within the pores provides by far the larger part of the active surface as the porous material will usually have a high BET surface of at least 50 m^2/g. Thus, the electrochemical process of this invention, i.e. the formation of nano particles, in particular nano crystals of the reaction product, will mainly take place in the pores of the electrochemically active material, in which supersaturation conditions may exist of the polyatomic ions or radicals which are formed during reduction of the oxidant gas. As a result, formation and growth of particles of the reaction product in the pores of the porous electrochemically active material will be limited by the dimensions of those pores. Depending on the nature of the porous material, the average diameter of the nano particles, in particular the nano crystals, will often be limited to a maximum of 5 nm. A dedicated choice of the electrochemically active material, in particular the pore size distribution of the electrochemically active material which is represented by the BET surface of the porous material, thus permits controlling the size of the nano particles, in particular the nano crystals of the reaction product, and thus the particle size of the reaction product.

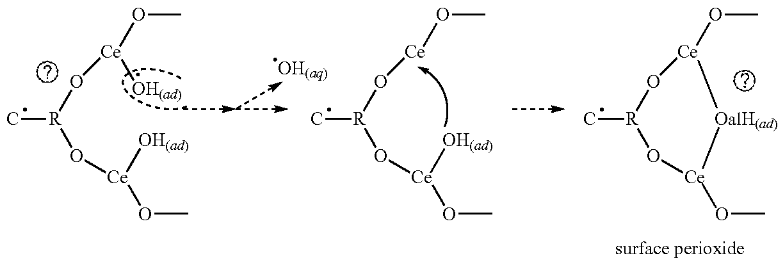
[0044] The electrochemical potential to which the gas-diffusion cathode is subjected, is a reducing potential relative to a reference electrode, preferably below the thermodynamic pH-potential equilibrium region of stability of the oxidant gas in water, more preferably below the region of thermodynamic stability of water but preferably not within the region of thermodynamic stability of hydrogen. This way the risk to the occurrence of water electrolysis to form hydrogen may be minimized. However, in certain embodiments the formation of hydrogen may be preferred, e.g. if the targeted application of the formed nano particles, in particular the nano crystals is related to in-situ hydrogen capture or storage.

[0045] The inventors have observed that the oxidized metal and/or metalloid cations formed in the process of this invention and outlined in the reaction schemes above, accumulate at the interface in the pores of the electrochemically active material, in a physical state which is different from the physical state of the surrounding liquid electrolyte, so that they may be separated therefrom. The reaction product may for example accumulate as particles of a product forming a solid or colloidal phase. Depending on the nature of the metal or metalloid cation, the reaction product may for example accumulate on the interface in the form of crystalline or amorphous nano particles, which may grow with time to take a larger size as the process proceeds and form a physical state which is different from the physical state of the electrolyte, so that the nano particles of the reaction product may be isolated from the cathode and the electrolyte. The reaction product may be released in a variety of physical forms, for example in the form of a precipitate, or in the form of colloidal nano particles, for example in the form of a colloidal dispersion. After having been released into the electrolyte, the particles may further aggregate to form a stable solid phase, a separable precipitate, gel-like, foam-like or a Pickering emulsion-like phase.

[0046] Since the nature of the forces with which the reaction product comprising the at least one metal element and/or metalloid element in an oxidized state adheres to or is adsorbed to the electrochemically active surface of the gas diffusion electrode may vary with the nature of that electrochemically active material and the nature of the oxidized compound, release of the reaction product in the form of nano particles, in particular nano crystals, into the electrolyte may occur as such, or may need to be forced.

[0047] Metal and metalloid elements may take various oxidation states and may form, with the species which result from the reduction of the oxidant gas, reaction products or compounds which contain one or more monoatomic or polyatomic ions, in an oxidation state which leads to a phase that may be separated from the catholyte and from the cathode. The skilled person will be capable of identifying those oxidized compounds which form a separable phase in a water based electrolyte, and select the appropriate electric (or redox) potential and pH for the catholyte which permits formation of a separable phase. Pourbaix "Atlas of electrochemical equilibria in aqueous solutions" second edition 1974 discloses the solubility and stability as ions or solid compounds of several metals and their oxides as a function of the voltage potential and the pH, at standard conditions. Theoretical diagrams for a wide variety of species can be constructed without undue burden based on the premises provided therein, included those for oxidant gases other than oxygen The skilled person is capable of identifying the electrochemical potential at which electrochemical reduction of the oxidant gas, and the corresponding oxidation of the metal cation or metalloid cation may occur. This is illustrated in FIG. **18**, which shows the electrochemical series of a few oxidant gases.

[0048] It has been observed that by varying the electric or electrochemical potential at the cathode, the chemical composition of the reaction product may be controlled. Without wanting to be bound by this theory, the inventors assume that the ionic or radical species of the oxidant gas may diffuse over the charged electrochemically active surface and cluster with other similar species, for example peroxide radicals, adhering to the active surface of the cathode.



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This clustering may lead to local super-saturation on the active surface of the electrochemically active material including the active surface within the pores of the electrochemically active material, and the growth of the ionic or radical species present on that electrochemically active surface (for example surface peroxide) into critical nuclei, as opposed to crystal formation in the electrolyte solution known from the prior art.

[0049] A dedicated selection of the pore size distribution of the electrochemically active material permits to obtain the nano crystals of the reaction product in a selected crystal form, and to affect their lattice parameters. In particular when use is made of an electrochemically active material having a quite uniform pore size distribution, nano crystals of the reaction product may be obtained which are monodisperse, or at least show a small particle size distribution curve. Within the scope of the present invention with monodisperse is meant, particles where 75% of the particles have a particle size which differs with maximum 5%, preferably maximum 3%, more preferably maximum 1%.

[0050] Although the electrochemically active surface of the cathode may contain adsorbed reactive radicals and/or adsorbed oxidant gas, and although the water based electrolyte may contain some dissolved oxidant gas, this will usually not be enough to ensure full recovery of all metal or metalloid ions present in the electrolyte. Supply of an oxidant gas to the cathode, in particular to the gas diffusion electrode, may therefore be preferred in order to ensure maximum recovery of the reaction product comprising the at least one metal or metalloid element in an oxidized state, from the water soluble precursor compound dissolved in the water based electrolyte and optimize the reaction rate. In practice, an oxidant gas supplied to the gas diffusion electrode will migrate from the hydrophobic side of the gas diffusion electrode, through the gas chamber of the gas diffusion electrode, towards, into and through the electrochemically active material of the gas diffusion electrode and cathode.

[0051] Examples of oxidant gases suitable for use with this invention include organic as well as inorganic oxidant gases. Example of inorganic gases suitable for use with this invention include ozone, oxygen, carbon oxide gases for example CO_2, nitrogen oxides for example NO, N_2O_3, halogen gases, halogen oxide gases, sulfur oxide gases, air, biogas, flue gas, acid gas and combustion exhaust gas and mixtures or two or more of the afore mentioned gases. Preferably however, use is made of air due to economic reasons. Other oxidant gases particularly suitable for use with this invention include those capable of forming oxidant mono-atomic radicals and/or oxidant polyatomic radicals, for example oxygen, ozone, carbon dioxide etc.

[0052] Particularly preferred oxidant gases are those which may be reduced so as to generate polyatomic ions, polyatomic radicals or polyatomic peroxides, for example those summarized in the table below:

perchlorate	ClO_4^{-1}	hydrogen sulfate	HSO_4^{-1}	hydrogen phosphate	HPO_4^{-2}
chlorate	ClO_3^{-1}	dihydrogen phosphate	$H_2PO_4^{-1}$	peroxide	O_2^{-2}
chlorite	ClO_2^{-1}	permanganate	MnO_4^{-1}	tetraborate	$B_4O_7^{-2}$
hypochlorite	ClO^{-1}	periodate	IO_4^{-1}	borate	BO_3^{-3}
Nitrate	NO_3^{-1}	hydrogen carbonate	HCO_3^{-1}		
Nitrite	NO_2^{-1}	sulfate	SO_4^{-2}		
bromate	BrO_3^{-1}	sulfite	SO_3^{-2}		
Iodate	IO_3^{-1}	carbonate	CO_3^{-2}		

[0053] The at least one oxidant gas is preferably selected such that one or more of the preferred polyatomic ions is generated, in particular one or more of the polyatomic ions selected from the group of acetate (CH_3COO^-), acetylide (C_2^{2-}), carbonate (CO_3^{2-}), peroxide (O_2^{2-}), phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), nitrate (NO_3).

[0054] According to another preferred embodiment, the at least one oxidant gas is selected from the group of organic gases, including ethers (e.g. ethylene oxide, propylene oxide), alkenes (e.g. ethylene, propylene), alkynes (e.g. acetylene), or conjugated dienes (e.g. butadiene) or mixtures of two or more of these gases. Ethylene oxide may for example be reduced at an electrochemical potential of −1.2V vs. SHE. For other organic gases the electrochemical potential may easily be determined by the skilled person.

[0055] The at least one oxidant gas may be used as such or in a mixture with one or more inert gases, for example N_2, Ar or He or a mixture of two or more of these gases.

[0056] The partial pressure of the at least one oxidant gas within the gas mixture is not critical to the invention and may vary within wide ranges. Yet, varying the oxidant gas partial pressure or the oxidant gas supply rate will permit to control the size of the crystals of the reaction product containing the at least one metal and/or metalloid element. Varying the oxidant gas partial pressure, in particular increasing or decreasing the partial pressure of the at least one oxidant gas, will also permit to control, in particular to increase or reduce the average lattice parameter of the reaction product crystals as measured by X-ray diffraction measured over a given crystallographic plane or measured using transmission electron microscopy imaging. Varying the oxidant gas partial pressure or the oxidant gas supply rate will namely affect the amount of oxidant gas that may accumulate on the electrochemically active surface, in particular by the amount of oxidant gas present on the active surface within the pores of the porous electrochemically active material. This amount of gas may in turn be controlled by controlling the gas supply rate to the gas chamber of the gas diffusion electrode, and by controlling the concentration of the oxidant gas in the gas that is supplied to the gas chamber of the gas diffusion electrode. When air is used as the oxidant gas, the flow rate will usually vary between 100 and 400 ml/min, preferably between 200 and 400 ml/min.

[0057] The concentration of the water soluble precursor compound in the electrolyte is not critical to the invention. However, the concentration of the water soluble compound is preferably at least 100 ppm. In general the concentration of the water soluble compound will not be higher than 10 g/liter as the efficiency of the process can hardly be improved at higher concentrations. Therefore, the concentration of the water soluble compound in the catholyte is preferably between 100 and 500 ppm. The concentration of the water soluble precursor in the catholyte may for example be varied by varying the rate with which the water soluble precursor is supplied to the catholyte. Such variation will in particular be done when variation of the particle size, in particular the crystal size of the reaction product is envisaged, since varying the concentration of the water soluble precursor permits varying the particle size, in particular the crystal size of the reaction product. The inventors have observed that the particle size, in particular the crystal size may increase with increasing precursor concentration or that the particle size, in particular the crystal size may decrease with decreasing precursor concentration.

[0058] The nature of the compound which may be recovered from the at least one water soluble precursor compound may be varied by selecting the appropriate oxidant gas. When O_2 or an O_2 containing gas is supplied as the oxidant gas, the compound will usually take the form of an oxide or a mixed oxide of the metal or metalloid ion. When CO_2 or a nitrogen oxide gas is supplied as the oxidant gas, the compound may take the form of a carbonate, a nitrite or a nitrate. In other words, the nature of the anion of the reaction product may be varied by a proper selection of the oxidant gas.

[0059] The skilled person will be capable of adapting the amount of oxidant gas supplied and the gas flow rate, to the concentration of water soluble precursor compound that needs to be isolated from the electrolyte. In particular, it may be desirable to vary the gas supply rate, in particular in case the process is operated in a continuous mode where a continuous supply of water soluble precursor compound to be removed takes place. Moreover, gas supply may create convective mass transfer in the catholyte and not only promote diffusion of the metal and/or metalloid ions from the water soluble precursor compound to the electrochemically active surface, but may also facilitate surface diffusion of reduction products of the oxidant gas, i.e. peroxide ionic and/or radical species, as well as surface diffusion of adhered metal and/or metalloid ions, or any intermediate reaction products, and thereby increase the reaction rate. Other suitable ways to create convective mass transfer comprise those known to the skilled person, for example the use of a stirrer, gas supply, the presence of a spacer material capable of creating turbulent flow conditions.

[0060] In a preferred embodiment, the porous electrochemically active material for the gas diffusion electrode and the cathode is chosen such that it has an active surface which comprises a plurality of active sites provided by surface functional groups, wherein the functional groups preferably contain one or more moieties selected from the group of a nitrogen containing moiety, an oxygen containing moiety, a chlorine containing moiety or a sulfur containing moiety.

[0061] To ensure maximum recovery, in a preferred embodiment, before supplying the cationic water soluble compound, the pH of the electrolyte in the cathode compartment is adjusted to a pH≤7.0, preferably a pH in acidic conditions, in which the formation of a solid reaction product would not be expected by the skilled person. More preferably, before supplying the water soluble precursor compound, the pH of the electrolyte is adjusted to a pH which is below the dissociation constant of the acid or salt of the water soluble precursor compound, more preferably below 5.0. Usually the pH will be at least 1.5 as below this value the process slows down too much. The inventors have observed that the pH of the catholyte gradually progresses towards alkalinity in the course of the reaction, which is often above the dissociation constant of the acid or salt of the ionic metal or metalloid compound. In particular the final pH of the catholyte may raise to a value of above 4, often above 6 or 7, more preferably above 9, most preferably above 11.

[0062] In a preferred embodiment of the method of this invention, an amount of a weak protonic electrolyte is supplied to the catholyte. The inventors have found that the metal oxidation rate may thereby be accelerated. Without wanting to be bound to this theory, the inventors believe that the weak protonic electrolyte acts as a catalyst or co-catalyst in the formation of reactive peroxide, ionic and/or radical species from the oxidant gas at the cathode and in the electrochemical reactions in which the water soluble compound is converted into a reaction product that may be separated from the cathode and the catholyte. The co-catalyst has been found capable of accelerating the oxidation of the metal cation or metalloid ion towards the separable compound, by accelerating the availability of reactive species. The inventors have further found that addition of the weak protonic electrolyte may not only increase the conductivity of the catholyte, but that it may also increase the current density over the cathode.

[0063] Moreover, the presence of the weak protonic electrolyte has the effect that variations in the pH of the catholyte in the course of the oxidation reaction, may be reduced to a minimum. This contributes to minimizing the risk to the occurrence of unwanted side reactions which would lead to the formation of compounds which could not easily be separated from the cathode and/or the catholyte and for example be water soluble. This separability provides an important advantage, as such a process may be suitable for use in or for direct coupling to isolate reaction products from processes employing biological material.

[0064] The amount of weak protonic electrolyte may vary within wide ranges but is preferably not less than a 10 mM solution and preferably not more than a 1.5 M solution, more preferably the concentration of the weak electrolyte varies between 10 and 500 mM, most preferably around 100 mM.

[0065] The weak protonic electrolyte may either be a weak protonic acid or a weak protonic base, depending on the pH range at which the separable compound may be formed. In particular, the weak protonic electrolyte may be a weak polyprotonic acid or a weak polyprotonic base.

[0066] A weak protonic acid is a protonic acid which only partially dissociates in water:

$$\mathrm{HA}_{(aq)} \leftrightarrow \mathrm{H}^{+}{}_{(aq)} + \mathrm{A}^{+}{}_{(aq)}$$

[0067] A weak polyprotonic acid is a weak acid which has more than one ionisable proton per molecule. The dissociation constant of a weak monoprotonic acid may be represented by the formula below:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

[0068] Preferred weak protonic acids have a pKa of between 2.0 and 8.0, preferably between 3.0 and 7.0, more preferably about 7.0. Examples of weak protonic acids suitable for use with the present invention include those selected from the group of weak organic and weak inorganic acids, in particular acetic acid, citric acid, oxalic acid, lactic acid, gluconic acid, ascorbic acid, formic acid, glycolic acid, potassium monohydrogen phosphate, potassium dihydrogen phosphate, ammonium chloride, boric acid, sodium hydrogen sulphate, sodium hydrogen carbonate, ammonium chloride, and mixtures of two or more hereof. Particularly preferred weak protonic acids are those having a pKa which is at least one unit higher than the pH of the catholyte.

[0069] Preferred weak protonic bases haves a pKa of between 6.0 and 12.0, preferably between 7.0 and 11.0. Examples of weak protonic bases suitable for use with this invention include those selected from the group of ammonia, trimethylammonia, ammoniumhydroxide, pyridine, the conjugated bases of acetic acid, citric acid, oxalic acid, lactic acid, gluconic acid, ascorbic acid, formic acid, glycolic acid, potassium monohydrogen phosphate, potassium dihydrogen phosphate, ammonium chloride, boric acid, sodium hydrogen sulphate, sodium hydrogen carbonate, or a mixture of two or more of the afore mentioned compounds.

[0070] To ensure maximum recovery as solid material, in a preferred embodiment the pH of the electrolyte in the cathode compartment is adjusted to acidic conditions, in which the formation of a solid phase is initially not anticipated. Later, the pH progressively turns more basic as the reaction progresses, wherein colloidal particles in suspension may become apparent.

[0071] In another preferred embodiment, an ionic water soluble salt is supplied to the catholyte, with the purpose of controlling, in particular of increasing the ionic strength of the catholyte. Salts of chloride with an alkali metal ion are preferred, NaCl being particularly preferred. However other electrolytes may be used as well. An amount of NaCl higher than 1 $g \cdot L^{-1}$ is preferred, more preferably the amount added will be higher than 10 $g \cdot L^{-1}$, most preferably at least 30 $g \cdot L^{-1}$.

[0072] The process of the present invention shows the advantage that the overall conductivity of the electrolyte in the cathode compartment, will vary to a minimum extent only in the course of the process. In particular, virtually no or only a minor decrease of the overall conductivity has been observed. This is probably due to adhesion or adsorption of cations containing the at least one metal element and/or metalloid element of the water soluble precursor compound, to the electrochemically active surface of the cathode, which in general is expected to attain a quasi stable level when all of the positive valenced ions to be isolated have been oxidized and transformed into a separable phase, especially in a batch-wise operated process.

[0073] Nevertheless, any unwanted variations in the conductivity may be compensated by supplying additional electrolyte or by incorporating into the catholyte a binary electrolyte. This may be of particular importance when the process of this invention is operated in a continuous manner, and continuous supply of metal and/or metalloid ions to be recovered takes place. By the presence of the binary electrolyte, the electrolytic conductivity may be increased to at least 5 $mS \cdot cm^{-1}$, more preferably between 20 and 80 $mS \cdot cm^{-1}$ and even more preferably between 20 and 50 $mS \cdot cm^{-1}$, and thereby the risk to a varying conductivity as a result of the removal of metal and/or metalloid ions may be minimised.

[0074] In order to facilitate release of the nano particles, in particular the nano crystals, from the electrochemically active material and facilitate recovering of the precipitate, the cathode may be subjected to polarization reversal. Polarisation reversal may also be used to clean the cathode from any unwanted remainders adhering thereto. This will permit to recover from the solution at least 10% of the amount of metal or metalloid ion that had been supplied to the cathode, more preferably to recover at least 40% thereof and even more preferably to recover at least 80% thereof.

[0075] The electrochemical process of the present invention as described in the present application makes it possible to recover metal or metalloid ions or a cation containing such metal or metalloid element contained in the water soluble precursor compound. Thereby recovery rates may be substantially complete, and amount to more than 99.0 wt. % thereof. Recovery rates will usually be at least 20 wt. % of the initial concentration of the at least one metal or metalloid element present in the precursor compound, preferably at least 50 wt. %, more preferably at least 80% and most preferably more than 90 wt. % or even more than 99% thereof.

[0076] The electrochemical process of the present invention is suitable for recovering components of a wide variety of water soluble precursor compounds, in a wide variety of concentrations.

[0077] The present invention is suitable for isolating a wide variety of compounds from an aqueous solution of the corresponding water soluble precursor compound. The precursor compound may for example be a compound of an ion of an element selected from the group of group II, III and IV elements of the periodic table of elements, C and Si excluded, the majority of the transition metal elements, the actinides and the lanthanides. The water soluble compound may also be a compound of an ion of an element selected from the group of group I elements when in a compound also containing P or S. The water soluble compound may also be a metal organic compound or complex, or an organic compound.

[0078] In a preferred embodiment, the at least one precursor water soluble metal compound is selected from the group of precursor compounds containing one ore more alkali metal ions, preferably one or more of Li, Na, K, Cs ions, more preferably Li and/or Na. In a second preferred embodiment, the at least one precursor water soluble ionic metal compound contains at least one metal ion selected from the group of alkaline earth metals, in particular preferably Ca and/or Mg. In a third preferred embodiment, the at metal ion contained in the least one precursor water soluble ionic metal compound is selected from the group of transition metals, preferably one ore more of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Pd, Ag, Cd, Hf, Ta, Tu, Re, Ir, Pt, or Au ions, more preferably one or more of V, Mn, Co, Nb, Ag, Pt or Au ions. In a fourth preferred embodiment, the at least one metal ion is selected from the group of post-transition metals, in particular one or more of Al, Ga, In, Sn, Tl, Bi ions. In a fifth preferred embodiment, the at least one precursor water soluble ionic metalloid compound is selected from the group of B, Si, Ge, As, Sb, Te, Se or C ions or mixtures of two or more hereof. In a sixth preferred embodiment, the at least one precursor water soluble ionic metalloid compound is selected from the group of Li, Na, Ca, Fe, Mg, Al or Zr ions. In a particularly preferred embodiment, the metal and/or metalloid ion is selected from the group of wherein the monoatomic cation is selected from the group of H^+, Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Ag^+, Zn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Cu^+ and mixtures of two or more hereof. Although the majority of the afore mentioned metal and/or metalloid ions may be used as such within the process of this invention, for some of them, in particular Na and K may need to be used in a mixture with a further metal and/or metalloid ion.

[0079] The water soluble precursor compound may be supplied as a precursor compound comprising one single type of metal or metalloid ion or element with a positive valence, but it is within the scope of this invention that a composition comprising a mixture of two or more metal ions or metalloid ions or elements with a positive valence may be supplied as well. In case a single metal or metalloid ion is supplied, the reaction product that may be separated from the aqueous precursor solution is preferably a compound comprising one single metal or metalloid in an oxidized state. In case the electrolyte comprises a mixture of two or more metal or metalloid ions or elements with a positive valence, the reaction product may comprise a mixture of compounds of the in an oxidized state, all reaction products for example responding to the formula M_xO_y, but it may also comprise mixed metal or metalloid compounds for example $M_xN_zO_y$. It is however also within the scope of this invention that a matrix comprising one a precursor compounds is supplied or a matrix containing a mixture of two or more precursor compounds.

[0080] In a first embodiment of this invention, the reaction product that is formed from the precursor compound may contain crystalline oxide nano particles, for example, but not limited to CeO_2, La_2O_3, Co_2O_3, Al_2O_3, Cs_2O, Li_2O, $CoFe_2O_4$, $FeAsO_4$, or non-stoichiometric forms thereof or hydrated forms thereof (e.g. $CeO_{1.75}$). In a second embodiment, the reaction product may contain crystalline carbonate nano particles, preferably but not limited to $Na_3La_3(CO_3)_5$, $NaHCO_3$, or non-stoichiometric forms thereof or hydrated forms thereof. In a third embodiment of this invention, the separable compound may contains a mixture of amorphous or crystalline metal oxide nano particles or mixed oxides. In a fourth embodiment of this invention additional ionic compounds may be supplied to the catholyte such as ionic liquids. As a result of the presence of such an ionic liquid the structure of the reaction product may comprise the ionic liquid products of its decomposition, for example but not limited to terbutylammonium chloride or terbutylammonium chloride. Surprisingly it has been found, and this has been confirmed by IR spectra of the reaction product formed—although the structure is not fully understood, that by supplying an ionic liquid a foamy reaction product is obtained.

[0081] The particles of the reaction product may be released in a variety of physical forms, for example in the form of colloidal nano particles, for example in the form of a colloidal dispersion, a separable precipitate of particles or a gel-like, foam-like or Pickering emulsion-like phase. Usually a stable dispersion or gel will be obtained. In order to improve the stability, the dispersion or suspension of the particles may be subjected to sonication or ultrasonication. According to another variant, one or more additives may added to the water soluble precursor compound, the electrolyte at the cathode, the suspension or dispersion at any convenient point of time. The additives may be selected from the group of dispersants, stabilizers, surfactants, polymers, copolymers, emulsifiers, cross-linking agents, capping agents and free flow agents or mixtures thereof. Such addition may done to stop growth of the nano particles in particular the nano crystals, to reduce the risk to agglomeration of the nano particles, to provide a stable dispersion.

[0082] In a preferred embodiment of this invention, the electrochemically active material of the gas diffusion electrode which forms part of the cathode preferably comprises an active surface having a plurality of active sites with a weak protonic acid functionality, i.e. active sites which only partially dissociate in water. Various electrochemically active materials may be used to achieve this. Preferred are those materials which have a surface comprising protonic acid functional groups. Particularly preferred are those materials which comprise electrically conductive particles of carbonaceous origin, more preferably those comprising electrically conductive particles of carbonaceous origin with a catalytically active surface comprising a plurality of protonic acid groups. It is believed that the protonic acidic functional groups present on the catalytically active surface, in particular acidic functional groups of the type R—H, may partly dissociate at a corresponding pH. The inventors also believe that the thus dissociated surface groups C—R^{*-} have a high oxygen affinity and thus intervene in the oxidation of the metal ion or the metalloid ion.

[0083] As electrochemically active material, a wide variety of conductive materials may be used, but preferred are porous materials, in particular those which contain weak protonic acid functional groups. Examples of such materials are well known to the skilled person and include porous metals and metalloids, for example porous nickel or copper, porous carbon based materials, porous ion exchange resins, carbon aerogels, silicon, conductive polymers, conductive foams or conductive gels, among others. The use of a porous carbon based material as or in the electrochemically active surface is preferred, because of its catalytic activity in combination with a reasonable cost and abundant availability in comparison to other materials. Examples of suitable materials include graphite, carbon nanotubes, graphene, carbon black, acetylene black, activated carbon or synthetic carbons such as vulcan. Other electrochemically active materials suitable for use with this invention include carbonaceous materials the surface of which has been chemically modified to adapt its catalytic activity and compatibility with the reaction medium. Without wanting to be bound by this theory, it is believed that the presence of oxygen-containing functional groups support the oxidation reaction. Particularly preferred carbon materials have a surface with quinone-type functional groups.

[0084] Suitable porous material for use as the electrochemically active layer preferably have a high specific surface area as measured by the BET method described in ASTM D5665, in particular a BET surface area of at least 50 m^2/g, preferably at least 100 m^2/g, more preferably at least 200 or 250 m^2/g, most preferably at least 400 or 500 m^2/g, but those having a surface area larger than 750 or 1000 m^2/g or even more may be particularly preferred. Porous materials particularly suitable for use as the electrochemically active layer include particles of carbonaceous origin, also those having a small BET surface area, but preferred are those with a high specific surface area as measured by the BET method, in particular carbonaceous particles selected from the group of graphite, carbon nanotubes, graphene, carbon black, activated carbon or synthetic carbons. Preferred conductive carbonaceous particles have a BET surface area of at least 50 m^2/g, preferably at least 100 m^2/g, more preferably at least 200 or 250 m^2/g, most preferably at least 400 or 500 m^2/g, but those having a surface area larger than 750 or 1000 m^2/g or even more may be particularly preferred.

[0085] The activated carbon preferably has a particle size in the range of 75 to 300 microns, preferably from 100 to 250 microns.

[0086] Suitable porous material for use as the electrochemically active layer preferably form a continuous layer on the cathode. Thereto, use can be made of a polymer material which functions as a support for the electrochemically active material.

[0087] According to another preferred embodiment, the electrochemically active porous material is a solid which is dispersable or flowable in the water based electrolyte. Hereby, the solid may be made of one or more of the above described materials.

[0088] In the method of the present invention, preferably use is made of a cathode comprising a porous gas diffusion electrode, wherein one side of the gas diffusion electrode comprises a layer of at least one electrochemically active material active for or capable of catalyzing the reduction of oxygen to hydrogen peroxide. Preferred active materials have been described above. In order to increase the reaction rate, convective mass transfer may also be created at least in the cathodic gas compartment.

[0089] The process of the present invention is suitable for use in a wide variety of applications. The process of the present invention may for example be used to produce nano crystals of selected materials in a selected particle size distribution, with a selected crystal form, with selected lattice parameters. The process of the present invention may also be used to recover metal ions or metalloid ions from an aqueous solution, and provides a suitable method for recovering for example precious metals, in particular resulting from destruction of electronic materials, from aqueous solutions.

[0090] The reaction product obtained according to the present invention, in the form of nano crystals, may have a wide variety of uses. For example for reaction products containing cerium, the CeO_2 or sub-oxides such as $CeO_{1.75}$ may be formed which are particularly suitable for the scavenging of oxidizing agents such as oxygen or hydrogen peroxide. Their use as oxygen scavenging agents may be of particular interest to the electronics industry as additives for screen-sealing agents. Their use as hydrogen peroxide scavenging agents may be of particular interest to the cosmetic industry, for example but not limited to scavenging naturally-produced peroxides in hair follicles to prevent or revert white hair. Other compositions, for instance those issued with the reaction with ionic liquids may have use as hydrogen or CO_2 scavengers, among many other numerous applications.

[0091] The present invention also relates to a composition comprising at least one aggregate particle of nano crystals obtained by the above described process wherein, the nano particles in particular the nano crystals have a particle size, in particular a crystal size of between 0.2 and 30.0 nm. Where a crystalline product is obtained, the nano crystals will usually have a lattice parameter of between 1.0 and 18.0 nm, and any aggregate particles formed will have an average particle size of ≤30 nm. The reaction product may take the form of a dispersion of the reaction product in an aqueous medium, with a solids content of between 1.0 and 30.0 wt. %, preferably between 5.0 and 10.0 wt. %. The aqueous medium may comprise the electrolyte, water or an aqueous solution.

[0092] The present invention also relates to a method for selectively isolating at least one metal element or a metalloid element or two or more thereof from an aqueous solution comprising a water soluble precursor compound thereof, wherein use is made of the process as described above.

[0093] The present invention further relates to a device for recovering a metal element or a metalloid element or two or more thereof from at least one water soluble precursor compound comprising a metal element or a metalloid element or two or more thereof, in the form of one or more nano particles, in particular nano crystals of at least one reaction product, wherein the device comprises

- **[0094]** means for supplying the water soluble precursor compound at least partly dissolved in a water-based catholyte to a cathode compartment of an electrochemical cell, equipped with a cathode comprising a gas diffusion electrode, wherein the gas diffusion electrode comprises a porous electrochemically active material having a BET surface area of at least 50 m^2/g,
- **[0095]** wherein the catholyte has a pH which is smaller than the pKa of the water soluble precursor compound,
- **[0096]** means for supplying at least one oxidant gas to the gas diffusion electrode,
- **[0097]** wherein the cathode has an electrochemical potential which is such that it is capable of causing reduction of the at least one oxidant gas to one or more corresponding peroxide, ionic and/or radical reactive species capable of reacting with the metal element, the metalloid element or a cation comprising such a metal or metalloid element or two or more thereof, to form at least one nano particle, in particular at least one nano crystal of the at least one reaction product with an average crystallite size equal to or smaller than 30.0 nm.

[0098] The invention is further illustrated in the appending figures.

[0099] FIG. **1***a* shows a schematic representation of the experimental electrochemical half-cell reactor suitable for use with the present invention.

[0100] FIG. **1***b* shows the process of the present invention including the reactions and nano crystal formation within the pores of the electrochemically active material.

[0101] FIG. **2** shows the removal efficiency in % of Ce^{3+} ions from the bulk solution in the presence of N_2 supplied through the gas-diffusion cathode, in the absence of oxidant gas, of example 1.

[0102] FIG. **3** shows the electrochemical response in case no oxidant gas is supplied through the gas-diffusion electrode, but only N_2.

[0103] FIG. **3***a*: Frequency response obtained in example 1 by Electrochemical Impedance Spectroscopy (EIS) recorded at 20 mV amplitude, in the frequency range from 100 kHz to 3 mHz.

[0104] FIG. **3***b* shows the cyclic voltammetry response obtained at a scan rate of 1 $mV \cdot s^{-1}$ in example 1.

[0105] FIGS. **3***c* and *d* show typical EIS responses for diffusional limitation across a film of infinite thickness (left) and limitations by finite diffusion through a film with fixed amount of electroactive substance, which once consumed is not replenished at the electrode or is only replenished very slowly (right), in example 1.

[0106] FIG. **3***e* shows a typical capacitive and pseudo-capacitive CV responses, in example 1.

[0107] FIG. **4** shows the extent of removal of the Ce^{3+} ions from the bulk solution in the presence of O_2 as the oxidant gas supplied to the gas diffusion electrode in example 1.

[0108] FIG. **5** shows the recovery efficiency (%) of the Ce^{3+} ions transformed into a solid product recovered as precipitate after being released from the electrode and sedimented in solution, in the presence of O_2 as the oxidant gas supplied through the gas-diffusion cathode, on the basis of dry weight of the recovered product, in example 1.

[0109] FIG. **6** shows the electrochemical response obtained for the experiments where air was supplied through the gas-diffusion electrode, in example 1:

[0110] FIG. **6***a* shows the frequency response obtained by Electrochemical Impedance Spectroscopy (EIS) recorded at 20 mV amplitude, in the frequency range from 100 kHz to 3 mHz.

[0111] FIG. **6***b* shows the cyclic voltammetry response obtained at a scan rate of 1 $mV\cdot s^{-1}$.

[0112] FIGS. **6***c* and *d* show typical EIS responses for adsorption limited processes linked to charge transfer reactions.

[0113] FIG. **7** shows the crystallite size and lattice parameter found for the different initial Ce^{3+} concentrations studied, in example 1.

[0114] FIG. **7***a* shows the crystallite size (220) for CeO_2 and NaCl.

[0115] FIG. **7***b* shows the lattice parameter CeO_2 and NaCl. There was a limit in detection for both parameters at Ce below 20 mg.

[0116] FIG. **8** shows transmission electron micrographies evidencing the characteristic morphology of CeO_2 nano particles with crystallite sizes matching those obtained by XRD, in example 1.

[0117] FIG. **9** shows transmission electron micrographics evidencing the aggregation of the small crystalline nano particles of FIG. **8** into larger size nano particles, of example 1.

[0118] FIG. **10** shows the removal efficiency (%) of the different metal ions from the bulk solution in the presence of air supplied through the gas-diffusion cathode.

[0119] FIG. **11** shows a device suitable for carrying out the process of the present invention.

[0120] FIG. **12** shows High-resolution transmission microsocopy (HRTEM) of nanoparticles obtained with example 1.

[0121] FIG. **13** shows IR spectra of the precipitates obtained under different experimental conditions with TBAB (FIG. **13***a*) and IR spectra of the initially employed reagents for the TBAB experiment (FIG. **13***b*). The IR spectra for the TBAC cases are shown in FIG. **13***c*.

[0122] FIG. **14** shows nanocrystals precipitated in the presence of excess IL in Example 7 and under in-situ hydrogen electrosynthesis. Small bubbles in the size range of 0.1 mm were visible, occupying more than 10% of the volume of the material floating.

[0123] FIG. **15** shows the XRD pattern for the nano crystalline product obtained with TBAB **30**.

[0124] FIG. **16** shows the charge in Coulombs, consumed during the experiments carried out at different concentrations (molar ratios) of TBAB.

[0125] FIG. **17** shows TGA characteristic of the nanocrystalline product formed with TBAB in a molar ratio of 20.

[0126] FIG. **18** shows electrochemical series of a few oxidant gases, the current density distribution over different gas-diffusion cathode materials (different types of carbon), registered at different steady state reduction potentials.

[0127] A device suitable for carrying out the process of the present invention is shown in FIG. **11**. The device shown in FIG. **1** comprises an electrochemical cell, comprising at least one anodic compartment **5** and at least one cathode compartment **15**. If so desired a plurality of anodic and cathode compartments may be present as well. If a plurality of anode and cathode compartments is provided, they are preferably arranged in a unipolar arrangement, with a plurality of alternating positive and negative electrodes forming a stack separated by ion permeable membranes. In a unipolar design, electrochemical cells forming the stack are externally connected, the cathodes are electrically connected in parallel as well as the anodes.

[0128] The anode or anodes **1** are immersed in an anode compartment comprising an aqueous anolyte fluid **2**. The cathode or cathodes **10** are immersed in a cathode compartment comprising an aqueous catholyte fluid **12**. The anodic compartment and cathodic compartment are in fluid communication to allow transport of cations, in particular transport of protons from the anodic compartment to the catholyte compartment, and transport of anions from the cathodic compartment to the anodic compartment. As anolyte fluid, any anolyte considered suitable by the skilled person may be used. In particular any aqueous electrolyte, conventionally used in electrochemical reduction reactions may be used. The anolyte may for example comprise an aqueous solution of an electrolyte selected from the group of sulphates, phosphates, chlorides and mixtures of two or more of these compounds. The anolyte chamber may comprise a supply member for feeding anolyte fluid. The catholyte chamber may comprise a supply member for feeding catholyte fluid. The catholyte may be different from the anolyte, but anolyte and catholyte may also be the same. Suitable catholyte materials include those well known to the skilled person, such as an aqueous solution of an electrolyte selected from the group of sulphates, phosphates, chlorides and mixtures of two or more of these compounds

[0129] The anode and cathode compartment **5**, **15** may be made of any material considered suitable by the skilled person, but are preferably made of a polymeric material. Suitable materials include polyvinylidene difluoride (PVDF), polytetrafluorethylene (PTFE), ethylene tetrafluoroethylene (EFTE), polyvinylchloride (PVC), chlorinated polyvinyl chloride (CPVC), polyacrylate, polymethylmethacrylate (PMMA), polypropylene (PP), high density polytethylene, polycarbonate and blends or composites of two or more of these compounds.

[0130] The at least one anode and the at least one cathode compartment **5**, **15** are preferably separated from each other by an ion permeable membrane **11** to control exchange of cations and anions between both compartments. Preferred ion permeable membranes comprise synthetic polymer materials. The ion permeable membrane on the one hand ensures that cations, in particular protons, may migrate from the anode to the cathode compartment, and on the other hand serves as a gas barrier and therewith counteracts the occurrence of so-called chemical short cuts. The ion permeable membrane also counteracts the occurrence of a pH reduction of the catholyte in the cathodic compartment. Suitable materials for use as ion permeable membrane include polyvinyldifluoride (PVDF), polytetra-fluoroethylene (PTFE or Teflon), poly(ethene-co-tetrafluoroethene (EFTE), polyesters, aromatic polyamides, polyhenylenesulfide, polyolefin resins, polysulphone resins, perfltiolorovinyl ether (PFVE), tripropylene glycol, poly-1,3-butanediol or blends of two or more of these compounds, or composites containing one or more of these compounds and being obtained by dispersion of a metal oxide and/or a metal hydroxide in a solution of the polymer to increase the ionic conductivity. The ion permeable membrane may also comprise an ion exchange material if so desired.

[0131] To improve structural integrity, the ion-permeable membrane **11** separating the anode and cathode compartment **5**, **15** may be reinforced with a rigid support, for example a rigid support made of a sheet, a fleece, which may be woven or non-woven or otherwise made of a porous polymer or a web or a mesh of metal fibres or metal fibres arranged in a woven or non-woven structure.

[0132] The cathode **10** used in the device of this invention is preferably a gas diffusion electrode, to ensure a sufficiently high mass transfer of oxidant gas to the electrochemically active surface present at the cathode, and a sufficiently high reaction yield, taking into account the limited solubility of oxygen in water. The gas diffusion electrode is preferably a multilayered electrode comprising a current density distributor **3** for supplying electric current to an electrochemically active surface **4** deposited on top of the current distributor.

[0133] The electrochemically active material **4** is preferably a material which has a high electric conductivity. This permits the electrochemically active material to take away or bring the electron from and to the current density distributor.

[0134] The electrochemically active surface may be formed of any conductive materials or composite materials with a high surface area. Examples of such electrode materials include carbon, carbon nanotubes, graphite, carbon fiber, carbon cloth, carbon aerogel, graphene, metallic powders, for example nickel, metal oxides, for example ruthenium oxide, conductive polymers, and any mixtures of any of the above. It should be appreciated that the entire electrodes may be porous and conductive enough so that a substrate is not needed. It should also be appreciated that the substrate may be formed of a non-conductive material that is coated with a conductive coating, such as, for example, platinum, rhodium (Rh), iridium (Ir), or alloys of any of the above metals. The high surface area enables the voltage to be minimized. By contacting the porous portion with the ionic electrolyte, the apparent capacitance of the electrodes can be very high when charged.

[0135] The gas diffusion electrode that is used as the cathode **10** in the device of this invention preferably comprises a current density distributor **3**, which may be made of any material and form considered suitable by the skilled person. Preferably however, use is made of a mesh type current density distributor, having a mesh received in a circumferential electrically conductive frame or an array of several meshes. The current density distributor is connected to a source of electric energy along a current feeder, for supplying electrical energy to the current density distributor. The mesh comprises a plurality of electrically conductive paths. The mesh may be formed of any suitable metallic structure, such as, for example, a plate, a mesh, a foil, or a sheet having a plurality of perforations or holes. Furthermore, the mesh may be formed of suitable conductive materials, such as, for example, stainless steel, graphite, titanium, platinum, iridium, rhodium, or conductive plastic. In addition, the metals may be uncoated or coated. One such example is a platinum coated stainless steel mesh. In one embodiment, the mesh is a titanium mesh. In other embodiments, use is made of a stainless steel mesh, a graphite plate, or a titanium plate. The wording "mesh" is meant to include a square meshes with a substantially rectangular shape and orientation of the conductive wires and insulating threads, but the mesh may also be tubular, or a coil film, or a otherwise shaped three-dimensional materials. Still other types of meshes suitable for use with this invention include perforated sheets, plates or foils made of a non-conductive material, having a plurality of wires or threads of a conductive material interlaced in the direction parallel to the current flow. A further type of mesh suitable for use with the present invention includes lines/wires of a conductive material, which extend parallel to the current flow direction, printed on a perforated sheet, foil or plate.

[0136] One side of the current density distributor **3** may be coated with an electrochemically active surface **4** capable of catalyzing the reduction of the oxidant gas. The layer of electrochemically active material **4**, i.e. the layer which is catalytically active in the reduction of the oxidant gas as described above, is preferably applied to the side of the current density distributor facing the gas phase. The electrochemically active surface usually has an interface with the electrolyte on one surface (i.e. the side facing the current distributor) and a water repellant (hydrophobic gas diffusion) layer **13** on the other side.

[0137] The device preferably comprises a supply member for supplying an oxidant gas to the side of the cathode comprising the electrochemically active layer.

[0138] The cathode compartment may comprise, preferably on a side opposite the side of the cathode comprising the electrochemically active layer, an inlet for supplying at least one weak protonic electrolyte, preferably an aqueous electrolyte. Preferably the flow rate with which the weak protonic electrolyte is variable.

[0139] The electrochemically active surface **4** may be coated on the side facing the gas phase **13**, with a water repellant layer **13** or a hydrophobic gas diffusion layer to minimize the risk of water leaking through the electrode into the gas phase. This hydrophobic layer or water repellant layer **13** may also be deposited on top of the electrochemically active surface **4**. Suitable materials for use as the water repellant layer include polyvinyldifluoride (PVDF), polytetrafluoroethylene (PTFE or Teflon), PSU, but other materials considered suitable by the skilled person may be used as well.

[0140] The anode **1** used in the device of this invention may be a conventional electrode, or may be a gas diffusion electrode similar to the cathode. The pH of the anolyte is preferably acidic, preferably ≤7.0, more preferably ≤5.0, most preferably ≤3.0 but no lower than 1.5. The electrolyte will usually have an ionic conductivity of at least 1.0 mS/cm, but it may amount to 70-100 mS/cm in practice.

[0141] The invention is further illustrated in the examples below.

EXAMPLE 1

[0142] Materials and Methods

[0143] Chemicals

[0144] Activated carbon employed was Norit® SX1G from Norit Americas Inc. Fluorinated ethylene propylene resin (Teflon® FEP 8000) was obtained from Dupont. Crystalline ultradry $CeCl_3$ 99.9% (REO) ampouled under argon was received from Alfa Aesar. K_2HPO_4 was procured from

Merck. HCl at 35%, $CeN_3O_9.6H_2O$ 99.99% trace metal basis, and analytical grade KI were purchased from Aldrich. 50% NaOH, analytical grade potassium hydrogen phthalate (KHP), and analytical grade $(NH_4)_6Mo_7O_{24}.4H_2O$ were acquired from Merck.

[0145] Electrochemical Cell Setup

[0146] Experiments were performed in a half-cell electrochemical reactor (FIG. **1**). The cathode half-cell consisted of a cathode, a reference electrode and a counter-electrode. Ag/AgCl 3 M KCl (+200 mV vs SHE) was used as a reference electrode (Koslow Scientific), whereas a Pt disk fixed by laser welding over a titanium (Ti) plate was used as a counter-electrode. All potentials here reported stay true for the Ag/AgCl 3 M KCl reference electrode. Cathode and counter electrode were separated by liquid electrolyte and the separating membrane, Zirfon® (AGFA). Working and counter-electrode were separated from each other by a distance of 4 cm, whereas the membrane was accommodated right in the middle (at 2 cm from each electrode). The principal function of Zirfon® was to prevent oxygen eventually evolved at the counter-electrode from reaching the working-electrode. The electrodes and separator had a projected electrode surface area of 10 cm^2. Inert or reactant gas flows (N_2 or air, respectively) were fed through the cathode gas compartment on each individual experiment. Gas flow rate was set at 400 mL min^{-1} (excess) in all cases and an overpressure of 10 mbar was applied. Electrolyte feeds were independently circulated through the cathode and counter-electrode compartments with a dual-head peristaltic pump, at a flow rate of approximately 100 mL min^{-1} (Watson-Marlow). Both liquid and gas streams under these conditions were consistent with a laminar flow profile.

[0147] A schematic representation of the experimental electrochemical half-cell reactor is shown in FIG. **1***a*.

[0148] Gas Diffusion Electrodes

[0149] A multilayered VITO CORE™ electrode was used which consists of a current collector (metal gauze), an active layer made of activated carbon embedded in a porous polymer matrix, and a hydrophobic gas-diffusion layer. PVDF was used as polymer binder, both for the active layer and the hydrophobic gas-diffusion layer (GDL). The hydrophobic particles in the hydrophobic backing were FEP 8000. A typical GDL is composed of 50 wt % PVDF and 50 wt % FEP 8000. The composition of the active layer for the uncatalyzed cathode was 20% PTFE with 80 wt % activated carbon. Otherwise, a catalyzed electrode may be employed, e.g. it was 20 wt % PTFE with 76 wt % activated carbon and 4 wt % CeO_2, which may improve the efficiency of the process but is not essential to carry out the targeted synthesis.

[0150] Electrolyte Composition

[0151] Independent electrodes were tested as gas-diffusion cathodes, in presence of air or N_2 respectively, at the cathodic gas compartment. $CeN_3O_9.6H_2O$ was added to the cathodic electrolyte, composed of 30 g/L NaCl and 10 mM sodium acetate dissolved in demineralized water and adjusted at pH 2.7 with HCl. Sodium acetate is not essential to carry out the targeted synthesis, however it may impact its rate. Different concentrations of $CeN_3O_9.6H_2O$ were independently tested, as follows: 0 ppm, 100 ppm, 500 ppm, 1000 ppm, 2000 ppm, 3000 ppm, 5000 ppm and 10000 ppm. The electrolyte at the counter-electrode (anode) compartment remained the same, but without the addition of Ce. The experiments were carried out at room temperature (18±2° C.).

Electrochemical Operation and Characterization

[0152] A Bio-Logic VMP3 potentiostat/galvanostat and frequency response analyzer was used in order to perform the electrochemical measurements. EC-Lab v.10.23 software was used for data acquisition. Chronoamperometric experiments were carried out at −0.350 V vs the reference electrode during a period of 120 min. Within that period steady state was achieved. Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) were registered before and after the polarization, in order to indirectly evaluate the effectiveness of the metal recovery process.

[0153] During the CA experiments at −0.350 V the production of H_2O_2 after O_2 electrochemical reduction takes place with the electrodes and electrolyte here proposed. At these conditions, electrodeposition of metallic Ce is not expected, as the thermodynamic condition for Ce reduction in aqueous medium within the pH range here studied (as shown in the Pourbaix diagrams) would happen only at potentials lower than −2.7 V [Pourbaix, 1974]. Still, transport of dissociated Ce^{3+} ions towards the cathode is expected mainly by diffusion, with possible subsequent adsorption in the porous electrode active sites. Otherwise, water electrolysis to form hydrogen is not expected at the conditions of this example.

[0154] Electrochemical Impedance Spectroscopy (EIS) was recorded at the steady state polarization potential (−0.350 V) a frequency range from 3 kHz to 3 mHz, with 6 points per logarithmic decade, using an amplitude of 10 mV. Careful attention was paid to guarantee stability, linearity, causality and finiteness, so that reliable and valid impedance data were obtained. The EIS response was only recorded when the variation of current was detected to be <±10 pA during a period of at least one hour. The time of a whole impedance scan was of about 19 minutes. Linearity was verified by real time monitoring of non-distortions in Lissajous plots, which were observed via an on-line connected oscilloscope. Causality was ensured as spurious (noisy) data were not observed while recording EIS. Validity of the data was verified by using the Kramers-Kronig transforms. After the corresponding EIS measurements, CVs were recorded in 2 cycles at 1 mV s-1, in a potential range from −0.450 to 0.450 V vs Ag/AgCl. Only the second cycle of the CV is here reported. No IR drop correction was established for the experiments here performed.

Analysis of the concentration of H_2O_2

[0155] A spectrophotometric method was employed to determine the concentration of H_2O_2 in solution as disclosed by Aryal & Liakopoulou-Kyriakides 2013, 3:117. Reagent A was prepared by mixing 33 g KI, 1 g NaOH and 0.1 g $(NH_4)_6Mo_7O_{24}.4H_2O$ into 500 mL deionized water. This solution was kept in dark conditions to inhibit oxidation of I. Reagent B was prepared with 10 g KHP dissolved into 500 mL deionized water. The standard calibration curve (not shown) was prepared from known H_2O_2 concentrations from 0 to 3 mg L^{-1}, dissolved into the same electrolyte used for the experiments, without cerium. Further analysis was carried out by pipetting 3.0 mL of Reagent A, 3.0 mL of Reagent B and 3.0 of standard sample into a beaker. The content of the mixture was allowed to react for 5 minutes, before reading the absorbance of the solution at 351 nm [GSI Scientific Report. (2009) Helmholtzzentrum fiir Schwerionenforschung, 2010-1].

[0156] The concentrations calculated of H_2O_2 are the average of the quantitative results obtained with 5 averaged calibration curves, described by the following equation:

$$A_{351}=0.3687\ C_{H2O2}\ R^2=0.9991$$

Where C_{H2O2} refers to the concentration of hydrogen peroxide (mg L^{-1}) and A_{351} denotes the absorbance registered at 351 nm.

[0157] Beside the known concentrations, problem samples were obtained after the electrochemical characterization experiments and were analyzed through the same procedure as the standards.

X-Ray Diffraction

[0158] X-ray powder diffraction (XRD) experiments were carried out using diffractometer PANalytical X'Pert Pro with CuKα (λ=1.5405 Å) at 40 kV. The conditions were: 4 sec/step; step=0.04° and continuous scan. The wet precipitates were placed on a monocrystal. The samples were measured both wet and dry. Since there were no important variations between them only the values concerning the dry samples are reported here.

[0159] The identification of the crystalline phases was done by comparison with the database. The crystallite size (D) was calculated using Scherrer's equation (Eq. 8):

$$D = \frac{B\lambda}{\beta_{1/2}\cos\vartheta} \quad \text{Eq. 8}$$

where B is the Scherrer constant (0.89), λ is the wavelength of the X-ray beam (1.5405 Å), $\beta_{1/2}$ is the full width at half maximum of the diffraction peak and θ is the diffraction angle.

[0160] Independent aqueous solutions with fixed concentrations of NaCl and sodium acetate (CH_3COONa) were supplemented with varying concentrations of $Ce(NO_3)_3 \cdot 6H_2O$ (namely 0 $mg \cdot L^{-1}$, 100 $mg \cdot L^{-1}$, 500 $mg \cdot L^{-1}$, 1000 $mg \cdot L^{-1}$, 2000 $mg \cdot L^{-1}$, 3000 $mg \cdot L^{-1}$, 5000 $mg \cdot L^{-1}$, and 10000 $mg \cdot L^{-1}$, respectively). The pH of each electrolyte was fixed at 2.7, with HCl. A colourless solution was formed in all cases. A constant potential of −0.350 V vs Ag/AgCl (3M KCl) was applied to the said cathodes. At the gas-compartment, N_2 or air were supplied for each independent experiment, at a constant flow rate (~400 $mL \cdot min^{-1}$). Under such operational conditions water electrolysis is avoided; however, when air is supplied through the GDE, O_2 electrochemically reduces to H_2O_2, upon availability of protons and electrons.

[0161] The overall solution was considered to be electroneutral before the electrochemical polarization was applied. Given the high concentration of NaCl, ion transport by migration is unlikely to occur.

[0162] As soon as the electrical polarization was applied to the cathode, a gradient of electrochemical potential developed across the half-cell. Since the concentration gradients were initially absent, the transport of some positively charged ions was likely steered from the solution in equilibrium towards the surface of the porous cathode, which were thus captured by potential-modulated electrosorption and stored capacitively in the diffuse part of the electric double layer.

[0163] FIG. **2** shows the extent of transport of the Ce^{3+} ions (removal efficiency in %) from the bulk solution in the presence of N_2 supplied through the gas-diffusion cathode and in the absence of oxidant gas. The removal efficiency (%) was calculated as a function of the initial content of Ce^{3+} in solution ($Ce_{T,i}$/mg):

$$REM_{eff} = \frac{C_{T,i} - C_{T,f}}{C_{T,i}} \times 100\% \quad \text{Eq. 9}$$

$Ce_{T,f}$ (mg) stands for the final content of Ce^{3+} in solution.

[0164] When no Ce^{3+} was supplied in the aqueous matrix (0 ppm), as a consequence of the starting concentration gradient established, the transport of Na^+ within the porous electrode microstructure may have been prolonged by diffusion to the rest of the electrode porosity. Yet, Na^+ was available at its highest concentration in the bulk. Altogether this establishes diffusion from the bulk to the EDL in the overall porosity of the GDE as the rate limiting step for Na^+ transport, until a dynamic equilibrium was reached.

[0165] FIG. **3** shows the electrochemical response obtained for the experiments where no oxidant gas was supplied through the gas-diffusion electrode and only N_2 was provided. FIG. **3***a*: Frequency response obtained by Electrochemical Impedance Spectroscopy (EIS) recorded at 20 mV amplitude, in the frequency range from 100 kHz to 3 mHz. FIG. **3***b* shows the cyclic voltammetry response obtained at a scan rate of 1 $mV \cdot s^{-1}$. FIGS. **3***c* and *d* shows typical EIS responses for diffusional limitation across a film of infinite thickness (left) and limitations by finite diffusion through a film with fixed amount of electroactive substance, which once consumed is not replenished at the electrode or is only replenished very slowly (right). FIG. **3***e* shows a typical capacitive and pseudo-capacitive CV responses.

[0166] In FIG. **3**, the symbols given below relate to the indicated experiments:

[0167] ○ t_i, $C_{Ce^{3+},i}$=0 mg·L-1 Ce^{3+}.

[0168] ● t_f, $C_{Ce^{3+},i}$=0 mg·L-1 Ce^{3+}.

[0169] Δ t_0, $C_{Ce^{3+},i}$=10 g·L-1 Ce^{3+}.

[0170] ▲ t_f, $C_{Ce^{3+},i}$=10 g·L-1 Ce^{3+}.

[0171] The frequency response for this case, obtained by electrochemical impedance spectroscopy (EIS) was found to be typical of semi-infinite linear diffusion (see FIG. **3***a*), this is, unrestricted diffusion to the large porous cathode. In the high frequency range, EIS presented a shift from a typical constant phase element behaviour (at the beginning of the experiment) to a pseudo-transfer resistance behaviour (at the end of the experiment) which is characteristic of the occluded porosity [Kaiser et al (1976) Electrochim. Acta, 21, 539]. The response in cyclic voltammetry (see FIG. **3***b*) is characteristic of porous electrodes with pseudo-capacitive behaviour (see FIG. **3***c*), which confirms the capacitive storage of Na^+[Yang et al., 2003, J Electroanal Chem 540:159]; yet, the overall process is limited by diffusion. Although some Na^+ is indeed considered to be electrostatically adsorbed, virtually no changes were observed on its bulk concentration (seen as conductivity) due to the proportion between the small quantity of ions that can be actually electrosorbed at the EDL and those exceedingly available in the aqueous matrix.

[0172] Conversely, for the cases supplemented with Ce^{3+} (4 mg to 403 mg of Ce^{3+}, corresponding to the aforementioned concentrations of $Ce(NO_3)_3$ from 100 ppm to 10000 ppm) the frequency response was observed to be distinctive of limitations by finite diffusion through a film with fixed amount of electroactive substance, which once consumed is not replenished at the electrode or is only replenished very slowly (see FIG. 3*a*.

[0173] Although FIG. **3** only presents the EIS and CV data obtained for the systems without $Ce(NO_3)_3.6H_2O$ or those supplemented with 10 g·L-1 of $Ce(NO_3)_3.6H_2O$, the electrochemical behaviour is representative of all cases where N_2-flows at the cathodic gas compartment and where the electrolyte is supplemented with Ce^{3+} even at concentrations as low as 100 mg·L-1 of $Ce(NO_3)_3.6H_2O$.

[0174] The pH and conductivity were monitored at the catholyte, at the start and end of the experiments. For the cases where N_2 was supplied (Finding 1) the starting pH of 2.7 for each individual experiment increased in about 0.3±0.18 by the end of the experiments, whereas it slightly decreased as a function of concentration (in no case it decreased below 2.8±0.2). The starting conductivity for the case without Ce^{3+} (i.e. 30 $g \cdot L^{-1}$ NaCl+10 mM sodium acetate) was 49.7±0.6 and it remained quasi-stable by the end of the experiments (50.1±0.3). This shows that practically no variation in the concentration of NaCl could be achieved at such high NaCl concentrations. For the cases with Ce^{3+}, an ordinary increase of the conductivity was observed as a function of concentration, before polarization. In this case, the conductivity decreased slightly after the polarization treatment was applied, in good agreement with the removal efficiencies observed in FIG. **2**; this is, by the end of each experiment the conductivity approximately corresponded to that of the 30 $mg \cdot L^{-1}$ NaCl alone.

[0175] For the system where N_2 was passed through the GDE the average Ce^{3+} removal efficiency was 25.42±12.14% (see FIG. **2**). In the absence of oxygen or other oxidant gases the removed amount of metal ions (Ce^{3+}) is believed to be captured at the porous electrode structure mostly by ion-exchange at the surface functionalities which contained Cl, S and O groups as characterized by scanning electron microscopy and energy dispersive X-ray spectroscopy.

O_2 Supplied as the Oxidant Gas Through the Gas-Diffusion Cathode

[0176] VITO CORE™ cold-rolled gas-diffusion electrodes (GDE), made of porous activated carbon (NORIT SX 1G), were employed as. The specific surface area for the powder of which the electrodes are made is of about 1000 $m^2 \cdot g^{-1}$. Once shaped in the form of the porous electrode, the active carbon layer typically has a specific surface area as measured according to the BET method of between 621 $m^2 \cdot g^{-1}$ to 745 $m^2 \cdot g^{-1}$ (Alvarez-Gallego et al 2012 Electrochim Acta 82:415, Sharma et al., 2014 Electrochimica Acta 140 191)

[0177] FIG. **4** shows the extent of transport of the Ce^{3+} ions (removal efficiency %) from the bulk solution in the presence of O_2 as the oxidant gas supplied through the gas-diffusion cathode and flowing through the gas compartment and diffusing through the gas-diffusion electrode. In this case, about the entire amount of Ce^{3+} was removed from solution (average 99.47±0.53%), as shown in FIG. **4**. Contrary to the previous case, the removal efficiency does not increase as a function of the concentration of metal in solution, indicating that adsorption by ion-exchange is not the prevailing phenomenon as in a classical electrosorption case (see finding 1).

[0178] The removal efficiency when O_2 was supplied through the gas-diffusion cathode was much more significant than in the case where only N_2 was supplied.

[0179] Not only removal of Ce^{3+} ions from solution took place but also the formation of a stable solid phase. FIG. **5** shows the recovery efficiency (%) of the Ce^{3+} ions transformed into a solid product recovered as precipitate after being released from the electrode and sedimented in solution, in the presence of O_2 as the oxidant gas supplied through the gas-diffusion cathode, on the basis of dry weight of the recovered product.

[0180] The solid phase is composed of CeO_2 isotropic nanocrystals, as identified by XRD and microscopic evidence described later, which precipitated at the interface between the porous activated carbon gas-diffusion electrodes (GDE) and the adjacent aqueous electrolyte. These were initially identified as colloidal nano particles dispersed in solution, which aggregate and precipitate as the process keeps running. Some of these are released into the bulk electrolyte whereas others stay attached to the electrode and are only released after stopping or reverting the electric polarization.

[0181] Higher recovery percentages were obtained at lower Ce^{3+} concentrations. It should be noted that the low recovery efficiencies are not due to low conversion rates. The discharge of the crystalline nano particles was not done by other means than just reversing the flow. Those nano particles that could be collected within that reversal time are those which were quantified. In this case, polarization reversal increases recovery.

[0182] The intermediates, byproducts (e.g. an adsorbed form of superoxide $O_2^{\cdot-}{}_{(ads)}$) and the electrosynthesized H_2O_2 are believed to also play a role. The EIS behaviour was found to be typical of faradic reactions (charge transfer) coupled by adsorbed intermediates (Wu et al 2012 Chem Rev, 112:3959), as observed in FIG. **6***a*. The CV response (FIG. **6***b*) further indicated that the limiting process at the GDE at −0.350 V vs Ag/AgCl were not anymore capacitive ion-storage or electrosorption alone but an electrocatalytic reduction, presumably O_2 reduction to H_2O_2. This constitutes part of the proof that the process for the formation of the nano crystals does not occur in solution as a result of pH changes but at the electrode porosity as a consequence of the electrocatalytic reactions, as observed by the characteristic rate-limiting EIS response for adsorption that is linked to the formation of superoxide intermediaries in carbon materials. The latter response is namely not observed when non-porous metallic catalysts are incorporated in the gas diffusion electrode, as in that case the mechanism does not involve the adsorption of such superoxide radicals which trigger the supersaturation conditions within the pores of the electrochemically active material of the electrode.

[0183] FIG. **6** shows the electrochemical response obtained for the experiments where air was supplied through the gas-diffusion electrode:

[0184] FIG. **6***a* shows the frequency response obtained by Electrochemical Impedance Spectroscopy (EIS) recorded at 20 mV amplitude, in the frequency range from 100 kHz to 3 mHz.

[0185] FIG. **6***b* shows the cyclic voltammetry response obtained at a scan rate of 1 $mV \cdot s^{-1}$.

[0186] FIGS. **6***c* and *d* show typical EIS responses for adsorption limited processes linked to charge transfer reactions.

[0187] The symbols in FIG. **6** have the following meaning:

[0188] ○ t_i, $C_{Ce^{3+},i}$=0 mg·L-1 Ce^{3+}.

[0189] ● t_f, $C_{Ce^{3+},i}$=0 mg·L-1 Ce^{3+}.

[0190] Δ t_0, $C_{Ce^{3+},i}$=10 g·L-1 Ce^{3+}.

[0191] ▲ t_f, $C_{Ce^{3+},i}$=10 g·L-1 Ce^{3+}.

[0192] FIG. **7** shows the crystallite size and lattice parameter found for the different initial Ce^{3+} concentrations studied.

[0193] FIG. **7***a* shows the crystallite size (220) for CeO_2 and NaCl.

[0194] FIG. **7***b* shows the lattice parameter CeO_2 and NaCl. There was a limit in detection for both parameters at Ce below 20 mg.

[0195] FIG. **8** shows the steady state current density as a function of time for different oxygen-reducing gas-diffusion cathodes, with and without CeO_2 catalyst, after 120 min of electrocatalytic production of hydrogen peroxide. N: Norit, V: Vulcan-Norit, AB: Acetylene Black-Norit. All electrodes were composed of a combination of 80% carbon mixture and 20% polymer (PVDF).

[0196] The crystal size of the crystalline product varied in gradient as a function of the initial concentration of Ce^{3+}, but also proportionally to the concentration of H_2O_2 found in solution (FIG. **7***a*). At lower Ce^{3+} concentrations the crystal size of CeO_2 is smaller whereas as the concentration increases the crystal size is larger. The average crystal size for CeO_2 was 3.5+0.337 nm, whereas for NaCl it was 45.1275+0.337. This makes possible further separation either by re-dissolution of NaCl with a pH where CeO_2 is still stable, e.g. pH>10 or by size exclusion (e.g. screening) after drying. The lattice parameters observed in FIG. **7***b*, also varied as a function of initial Ce^{3+} ion concentration and proportionally to the concentration of H_2O_2 found in solution. It is possible that Ce^{3+} plays a co-catalytic role in the electrosynthesis of H_2O_2 itself.

[0197] FIG. **8** shows transmission electron micrographies evidencing the characteristic morphology of CeO_2 nano particles with crystallite sizes matching those obtained by XRD.

[0198] FIG. **9** shows transmission electron micrographies evidencing the aggregation of the small crystalline nano particles of FIG. **8** into larger size nano particles.

[0199] FIGS. **8** and **9** in fact show characteristic fingerprints of the materials formed by the method of this invention, whose properties can be tuned as per controlled variations in the physicochemical or electrochemical conditions provided.

[0200] To release the nano crystals from the electrochemically active layer of the gas diffusion electrode, several techniques may be used. Suitable techniques include reversing the polarity of the electrode, accelerating the electrolyte flow rate. The fact that these techniques cause release of the nano crystals into the catholyte, is an additional proof of the process taking place in the pores of the electrochemically active layer and not in the electrolyte solution. In fact, when comparing the size and morphology of the product obtained by just changing the pH of the electrolyte a difference is clear. Nano crystals are not obtained and instead an amorphous product is visible as appreciated by XRD. In addition, the nanocrystal product obtained by this invention shows a characteristic monodisperse foam-like morphology (see FIGS. **12** and **14** HRTEM) whereas the product obtained by simple addition of a base until an alkaline pH is reached shows high non-uniformity.

EXAMPLE 2

[0201] Independent electrodes were tested as gas-diffusion cathodes, in presence of air at the gas compartment (to provide O_2 for its reduction to H_2O_2, its polyatomic ions or radical). The reagents presented in Table A were dissolved in demineralized water and the pH of the solution where the pH was adjusted to approximately 4.

TABLE A

Composition of catholyte in demineralized water.

	Chemical name	Chemical formula	Quantity (mg · L^{-1})
1	Cerium nitrate hexahydrate	$Ce(NO_3)_3 \cdot 6H_2O$	350
2	Dysprosium nitrate x hydrate	$Dy(NO_3)_3 \cdot xH_2O$	80
3	Erbium nitrate pentahydrate	$Er(NO_3)_3 \cdot 5H_2O$	53
4	Europium nitrate pentahydate	$Eu(NO_3)_3 \cdot 5H_2O$	6
5	Gadolinium nitrate hexahydrate	$Gd(NO_3)_3 \cdot 6H_2O$	59
6	Holmium nitrate pentahydrate	$Ho(NO_3)_3 \cdot 5H_2O$	18
7	Lanthanum nitrate hexahydrate	$La(NO_3)_3 \cdot 6H_2O$	159
8	Lutetium nitrate hydrate	$Lu(NO_3)_3 \cdot xH_2O$	6
9	Neodymium nitrate hexahydrate	$Nd(NO_3)_3 \cdot 6H_2O$	206
10	Praseodymium nitrate hexahydrate	$Pr(NO_3)_3 \cdot 6H_2O$	51
11	Samarium nitrate hexahydrate	$Sm(NO_3)_3 \cdot 6H_2O$	53
12	Terbium nitrate hexahydrate	$Tb(NO_3)_3 \cdot 6H_2O$	12
13	Thulium nitrate pentahydrate	$Tm(NO_3)_3 \cdot 5H_2O$	8
14	Yttrium nitrate hexahydrate	$Y(NO_3)_3 \cdot 6H_2O$	536
15	Ytterbium nitrate pentahydrate	$Yb(NO_3)_3 \cdot 5H_2O$	50

Additionally, 30 g/L NaCl were provided and dissolved. The operational volume of the catholyte in each experiment was 125 mL.

[0202] The concentration of the different metals was quantitatively analyzed by means of ICP-MS.

[0203] The process was applied at constant polarization at −0.350 my vs the previously referred reference electrode for a period of 2 hours. After few minutes of processing (<20 min), the color of the electrolyte progressively shifted from transparent towards white in one appreciable turbid phase. The process showed a gradual change in pH up to 11. Current densities above 40 mA·cm^{-2} were registered under the constant cathodic polarization conditions. After the process was stopped, the solid particles formed aggregated and sedimented leaving a clear liquid medium and a separable solid precipitate phase.

[0204] Most of the metal content was found to be removed from solution (FIG. **10**), this is, >99.9 for all metals together, as determined by ICP-MS.

[0205] FIG. **10** shows the removal efficiency (%) of the different metal ions from the bulk solution in the presence of air supplied through the gas-diffusion cathode.

[0206] A mixed crystalline concentrate was obtained. In total, 91 mg of solid REE content were recuperated which correspond to about 25% of the total ionic (dissolved) REE content in the original aqueous matrix. The isolated products showed crystalline properties matching with crystallite sizes of 1.97 nm, 1.71 nm and 2.29 nm, respectively.

EXAMPLE 3

[0207] The composition of the electrolyte was identical to that explained for example 1, but lanthanum nitrate was used instead of cerium nitrate, in concentrations of 0 ppm, 100 ppm, 500 ppm, 1000 ppm and 5000 ppm.

[0208] The initial pH and conductivity of the catholytes containing the different concentrations of the metal are disclosed in Table b. The operational volume of the catholyte in each experiment was 125 mL.

TABLE b

Measured pH and conductivity of the catholytes with different concentrations of lanthanum nitrate $La(NO_3)_3{\bullet}6H_2O$ by the start of experimentation.

	Concentration (ppm)	0	100	500	1000	5000
Catholyte	pH	2.54	2.15	2.70	2.78	2.76
	Conductivity ($mS \cdot cm^{-1}$)	51.0	51.6	50.4	50.3	52
Anolyte	pH	2.8	2.8	2.74	2.74	2.74
	Conductivity ($mS \cdot cm^{-1}$)	49.7	49.7	49.8	49.8	49.8

[0209] The concentration of lanthanum was quantitatively analyzed by means of ICP-MS.

[0210] A colourless solution was formed when dissolving the chemicals. Air was supplied to the gas compartment. After 2 h of processing at constant polarization conditions of −0.350 V vs Ag/AgCl (3M KCl), the color of the electrolyte remained transparent throughout the experiment. However when stopping the polarization and reversing the flow, visible white turbidity was released into the medium. The amount of product released (or turbidity) corresponded to the initial concentration of lanthanum nitrate. After about an hour, all the turbid product had precipitated. The pH changes were similar to those observed in the catholyte in example 1, the pH of the catholyte significantly increased by the end of the experiments where air was supplied through the gas diffusion compartment. The conductivity and pH of catholyte and anolyte, remained almost the same. An overall slight decrease in catholyte conductivity could be debated.

TABLE c

pH and conductivity of the catholytes for different concentrations of $La(NO_3)_3{\bullet}6H_2O$ at the end of the experiment.

	Concentration (ppm)	0	100	500	1000	5000
Catholyte	pH	11.5	12.47	11.62	11.8	5.37
	Conductivity ($mS \cdot cm^{-1}$)	49.1	49.9	51.6	50.7	47.4
Anolyte	pH	2.37	2.78	2.23	2.20	2.68
	Conductivity ($mS \cdot cm^{-1}$)	49.7	49.9	50.7	49.5	47.5

The clear solution and the solid white precipitate were separated and analyzed. For all cases >99.9% of lanthanum had been removed from the solution. When analyzing the white precipitate by XRD, the produced solid showed characteristics of crystalline nano particles matching those of burbankite and more specifically lanthanum remondite, this is $Na_3La_3(CO_3)_3$. An amorphous phase was additionally detected.

EXAMPLE 4

[0211] The composition of the electrolyte was identical to that explained for example 1 but instead of cerium nitrate a boric acid was supplied in the catholyte. The concentration of boric acid was kept constant for all experiments (5 $g{\cdot}L^{-1}$). The effect of the polarization potential was evaluated. The following potentials vs. the reference electrode were compared: −0.350 V, −0.550 V, −0.750 V, −0.950 V. The operational volume of the catholyte in each experiment was 125 mL.

TABLE D

pH and conductivity of the catholyte at the start of experimentation at different cathode potentials.

		Applied potential (V vs Ag/AgCl 3M KCl)				
		−0.150	−0.350	−0.550	−0.750	−0.950
Catholyte	pH	2.67	2.63	2.51	2.51	2.76
	Conductivity ($mS \cdot cm^{-1}$)	47.1	47.4	47.2	47.4	46.9
Anolyte	pH	2.74	2.74	2.8	2.8	2.8
	Conductivity ($mS \cdot cm^{-1}$)	49.8	49.8	49.7	49.7	49.7

[0212] From the changes in the pH and conductivity, especially of the catholyte, it can be observed that the same trend found in previous examples was observed; this is, the pH significantly increased throughout the experiment. However, only in the case at −0.950 V a visible colour change of the electrolyte towards yellow could be observed.

[0213] The shift in pH was directly correlated to the applied potential. The pH change took place during the first hour of the experiment and even increasing further the time of polarization (i.e. from 2 to 4 h) did not result in pH variations to higher magnitudes.

TABLE E

Measured pH and conductivity of the catholytes by the end of experimentation at different applied cathode potentials.

		Applied potential (V vs Ag/AgCl 3M KCl)				
		−0.150	−0.350	−0.550	−0.750	−0.950
Catholyte	pH	5.37	6.55	6.92	8.45	8.5
	Conductivity ($mS \cdot cm^{-1}$)	45.2	46.6	46	44.1	45
Anolyte	pH	2.68	2.13	2.15	2.13	2.15
	Conductivity ($mS \cdot cm^{-1}$)	47.5	51.0	50.3	50.5	50.8

After centrifugation and drying, a crystalline product could be recuperated matching the characteristics of sassolite, except for that formed at −0.950 V which had characteristics of nanocrystalline borax $Na_2B_4O_7.10H_2O$. The latter product may have application as dopant in flexible and fluorescent electronics. The example below show the electrochemical series showing the reduction potential of different oxidizing gases to peroxides or their polyatomic ions or radicals. The potentials reported in this table refer to the normal hydrogen electrode (NHE). These potentials are calculated by Nernst equation.

TABLE F

Redox pair (half-cell reaction)	Thermodynamic reduction potential of the half-cell reaction at pH 1 (V vs NHE)
NO/NO_3^-	+0.958
O_2/H_2O_2	+0.547
$O_2/HO_2\bullet$	−0.13
$CO_2/HOOCCOO^-$	−0.43
CO_2/HCO_2^-	−0.49
$CO_2/HCOO^-$	−0.61

EXAMPLE 5

[0214] Eight different electrolyte compositions were tested, as described in example 1 but instead of cerium nitrate, the following independent compounds were supplemented the catholyte in a concentration of 500 ppm, respectively:

[0215] 1. $Co(NO_3)_2.6H_2O$

[0216] 2. $Al(NO_3)_3.9H_2O$

[0217] 3. CsCl

[0218] 4. LiCl

[0219] 5. KNO_3

[0220] 6. $Sm(NO_3)_3.6H_2O$

[0221] 7. $Er(NO_3)_3.5H_2O$

[0222] 8. $Lu(NO_3)_3.xH_2O$

[0223] 9. $Fe(NO_3)_3$

[0224] The process was carried out at −0.350 V. The operational volume of the catholyte in each experiment was 125 mL. In all cases, a nano crystalline product could be recovered except for KNO_3. On each case where a precipitate was found, the latter had characteristics (color, morphology) associated to the specific precursor employed, proving that nano crystalline materials can be formed with a wide diversity of metals from different groups in the periodic table. In all cases the crystallite size was <30 nm.

EXAMPLE 6

[0225] A catholyte was prepared, identical to that explained for example 1 but instead of cerium nitrate, arsenic acid was employed in a solution containing 72 g/L of arsenic and iron chloride considering a Fe/As ratio of 1.5 and sulfuric acid considering 5.61 g/L of S. The process was carried out in the same experimental conditions as example 1 but at an operational temperature≥80° C. After processing, stable nanocrystalline scorodite was obtained, with a crystallite size<30 nm. This embodiment may be applicable to arsenic immobilization.

EXAMPLE 7

[0226] Experimental Conditions

[0227] In the present example, the process claimed was studied under the presence of ammonium-based ionic liquids (IL). More specifically, Tetrabutylammonium bromide (TBAB) and tetrabutylammonium chloride (TBAC) were employed. There are few literatures showing the use of ILs for the synthesis of metal organic frameworks (MOFs) by ionothermal synthesis (Lei Liu, David S. Wragg, Hongyan Zhang, Ying Kong, Peter J. Byrne, Timothy J. Prior, John E. Warren, Zhuojia Lin, Jinxiang Dong and Russell E. Morris. Ionothermal synthesis, structure and characterization of three-dimensional zinc phosphates. Dalton Trans., 2009, 6715-6718.). Few literatures also report that nanoparticle-stabilized ILs may behave as Pickering emulsions in water (Huan Ma and Lenore L. Dai. Particle Self-Assembly in Ionic Liquid-in-Water Pickering Emulsions. Langmuir, 2011, 27 (2), pp 508-512) i.e. they assemble themselves to fom cage-like structures wherein some gas may be trapped in. These emulsions are typically stable as long as the medium is undisturbed. Otherwise ILs can be used as electrolytes due to their conducting properties (Chiappe and Rajamani 2012; Chiappe et al 2011 and Andrzej Lewandowski, Agnieszka Świderska-Mocek. Ionic liquids as electrolytes for Li-ion batteries—An overview of electrochemical studies. Journal of Power Sources. Volume 194, Issue 2, 1 Dec. 2009, Pages 601-609.). All reagents were used as purchased without further purification.

[0228] Demineralized water was used throughout the study. Activated carbon employed was Norit® SX1G from Norit Americas Inc. Fluorinated ethylene propylene resin (Teflon® FEP 8000) was obtained from Dupont. Two ILs based on ammonium base i.e. TBAB (Sigma-Aldrich ≥98.0%) and TBAC (Aldrich ≥97.0% (NT)) were purchased. Lanthanum nitrate hexahydrate ($La(NO_3)_9.6H_2O$) was also purchased from Aldrich® (99.99% trace metals basis). All reagents were stored as per recommendations of the corresponding supplier. Handling of all reagents was carried out as per recommendations in the corresponding Material Safety Data Sheets (MSDS). Experiments were performed in a half-cell electrochemical reactors equivalent to those described in example 1, unless otherwise specified. The principal functions of Zirfon® here were to prevent oxygen eventually evolved at the counter-electrode from reaching the working-electrode, to serve as ion permeable separator, and also as a fluid transport barrier to maintain the desired pH at the catholyte compartment. The electrodes and separator had a projected electrode surface area of 10 cm^2. The reacting (oxidant) gas flows (air or CO_2, respectively) were fed through the cathode gas compartment on each individual experiment. Gas flow rate was set at 200 mL/min (excess) in all cases and an overpressure of 30 mbarg was applied. Electrolyte feeds were independently circulated through the cathode and counter-electrode compartments with a dual-head peristaltic pump, at a flow rate of approximately 20 rpm (Watson-Marlow). An acidic basal electrolyte was employed in all experiments related to this example, consisting of demineralized water supplemented with HCl to achieve a starting pH of 2.7. The effect of two independent oxidant gases was investigated, aka air (composition is Nitrogen: 78%; Oxygen: 20%; CO_2: 0.03%, inert gases mainly argon: 0.97%; water vapor: 1%) and CO_2/N_2 80%/20%, respectively. $La(NO_3)_3.6H_2O$ was added to the cathodic electrolyte, at a concentration of 500 ppm. Different molar ratios between the IL and $La(NO_3)_3.6H_2O$ were investigated, as follows: 0, 0.1, 1, 10, 20, 30 and 86.5. The last molar ratio corresponds to a concentration of 0.1 M for the ILs. The electrolyte at the counter-electrode compartment (anodic) was identical to that of the catholyte (acidic basal electrolyte), but without the addition of lanthanum nitrate or IL.

[0229] The experiments were carried out at room temperature (18±2° C.). The parameters like H_2O_2 concentration, conductivity and pH were measured before and after each experiments in both the sets. Three more cases were carried out where catholyte was acidic basal electrolyte only, $La(NO_3)_3.6H_2O$ in acidic basal, TBAC (0.1 M). At higher concentrations of TBAB (specially 0.1 M) gave yellow precipitates or by-products in the anolyte chamber which may be some compounds of bromide or nitrate. Using only TBAB (0.1 M) without the metal nitrate in acidic basal electrolyte did not show positive results as the potential did not reach to −0.95 V vs Ag/AgCl. At the highest concentration for both TBAB and TBAC the experiments were carried out at −0.35 V vs Ag/AgCl. A Bio-Logic VMP3 potentiostat/galvanostat and frequency response analyzer was used in order to perform the electrochemical measurements. EC-Lab v.10.40 software was used for data acquisition. One linear scan voltammetry (LSV) from 0 to −0.950 V followed by chronoamperometry (CA) experiments were carried out at −0.950 V vs Ag/AgCl until pH 11 was reached. The concentration of La was quantitatively analyzed in samples from the catholyte and anolyte solutions, respectively, by means of ICP-MS. First, the sample solutions were pipetted from the supernatans. Each sample was diluted by a factor x and acidified prior to analysis. For the 10× dilution case, 1 ml of sample solution was mixed with 1 ml HNO_3 and the result diluted to 10 ml with Milli-Q water. For the 100x dilution case, a dilution to a final volume of 100 ml was used. Calibration of the observed ion intensities was performed against a series of calibration standards prepared on the basis of a 1000 mg/l Merck, Certipur, Cat No 1.70311.0100, $Ce(NO_3)_3$ solution in 2-3% HNO_3. Calibration standards of 0, 1, 2, 5, 10, 20 ppb, 100, 200, 500, 1000 and 2000 ppb were prepared. All measurements were performed with a Varian 820 ICP-MS. On a daily basis, a mass calibration was performed; ion lenses and gasflows were optimized to obtain a maximal signal-to-noise ratio with a 10 ppb multi-element standard provided by Varian.

[0230] The catholyte conductivities measured before the individual different experiments carried out are presented in Table 1. By the end of the all experiments the conductivity decreased sifnificantly, which was linked to a decrease in both the amount of IL present in the electrolyte as well as on the La concentration in the electrolyte (Table G2). The IL present in the electrolyte was removed from the electrolyte 60-75% in all cases and partly found in the precipitates. However, after the precipitates were washed with distilled water, most of the IL there present was was washed out.

TABLE G

Initial and final conductivities of the catholytes employed for the different experiments.

Experimental condition	Initial conductivity (mS/cm)	Final conductivity (mS/cm)
No IL added	0.853	No change
TBAB 10	1.885	0.095
TBAB 20	2.72	0.190
TBAB 30	3.57	0.280
TBAB 86.5	7.57	0.300
TBAC 10	1.873	0.116
TBAC 20	2.78	0.160
TBAC 30	3.38	0.375
TBAC 86.5	7.56	0.378

Besides the IL, mg/L quantities of formic and acetic acid were found, without having a particular correlation with the amount of IL added. The inventors believe that the formic and acetic acid quantified are issue from the reduction of CO_2 or from the partial degradation of the IL. The inventors also believe that these products may serve as linkers between the IL or its degradation products and the nanocrystal products formed within the process, in a similar way to what takes place in the more classical electrochemical formation of MOFs. The product formed at −0.350 V has the appereance as classical precipitates. The formation of the product at −0.350 V was compared to that formed at at −0.950 V. As shown by the IR spectra in the FIGS. **13***a, b* and *c*, the characteristic response and thus the characteristic bonds of the product are identical and only differ in intensity in correlation with the IL concentration employed and not by the type of IL. It is also shown that only part of the IL characteristic bonds remain in the precipitate, suggesting that at least part of the IL remains forming part of the structure of the precipitate product. The IR of the precipitate samples were compared before (P2) and after (P3) washing, showing the removal of an excess of IL but still after washing the structural effect of part of the IL remains. Thus, the product formed is believed to be a metal-organic compound with characteristics of both the IL and the nanocrystals.

[0231] From the above IR spectra of FIGS. **13***a, b* and *c* respectively the inventors could interpret that peak a is related to the bonding of lanthanum and nitrogen in case of original La-nitrate. This peak becomes broader when lanthanum is bonded to nitrogen of TBA. Peak b relates to N—CH_2 bonding. This peak however appears in the first Figure (unwashed part) but disappears in the second Figure indicating that some TBAB molecules that lied as surfactants on these compounds. The peak c (many peaks) are seen in case of original TBAB (lower blue curve in FIG. **13***b*). These refer to the C—N bonds in aliphatic amines. In the Figure corresponding to the washed samples (P3) it can be observed that some of these peaks are lost however not all indicating that there are some changes in the bonding between the nitrogen and methylene groups.

[0232] It should be noted that under the polarization condition applied at −0.950 V, hydrogen formation is also possible. Under this condition, the precipitates still looked initially as discrete precipitates, however, it was noticeable that they allow the sequestration of the hydrogen formed in situ and ultimately form a foam-like product that floats over a column of the catholyte due to the hydrogen it carries (see FIG. **14**). It is believed by the inventors that this product behaves similarly to a Pickering emulsion where the nanocrystals formed stabilize the remaining IL by self-assembly in solution, forming the characteristic cage-like structures where the gas can be sequestrated. The product also showed the characteristic of Pickering emulsions of stability until the medium is perturbed by simple agitation. Under such condition the hydrogen bubbles are released back into the air. The amount of hydrogen sequestrated in the nanocrystalline product formed was estimated to be above 10% in volume with respect to the solid precipitate.

[0233] FIG. **14** shows nanocrystals precipitated in the presence of excess IL and under in-situ hydrogen electrosynthesis. Small bubbles in the size range of 0.1 mm were visible, occupying more than 10% of the volume of the material floating.

The XRD patterns of the precipitate product washed were registered. Although the XRD pattern did not correspond to any correspondence in the databases available, the product showed characteristic features of high crystallinity and of a nanomaterial with small crystallite size (e.g. <10-5 nm). A characteristic XRD spectrum is shown for TBAB **30** in FIG. **15** below.

[0234] The characterization by scanning electron microscopy (SEM) showed N, C, La and O and in the precipitate elemental analysis, with a strong correlation in position, being a second indicator of the structural incorporation of at least part of the IL in the nanocrystals. Br and Cl from the IL were also found but lost when the precipitate was washed. The elemental analysis of the products formed showed an approximate proportion of 1:1 of hydrogen and carbon.

[0235] Based on the electrochemical response obtained, the charge consumed for each experiment was quantified, the results are shown in FIG. **12**. An exponential correlation between the charge consumed and the IL concentration employed was found, indicating that the IL indeed takes part on the electrochemical process.

[0236] The TGA characterization (see FIG. **12**) of the precipitates obtained indicate that the nanocrystalline product contains not the full ionic liquid but only fractions of it, which may be incorporated after partial degradation of the IL during the process. It is believed that the polyatomic ion radicals issued from the reduction of the oxidizing gas contribute to this IL degradation process and ultimately on the linkage of the IL fractions to the final precipitate structure. Although the structure of the nanocrystalline product cannot be fully established at this moment, the authors support the rationale that at least part of IL is found in the final nanocrystals, these being a metal-organic product.

[0237] More than 83% of the initial La precursor could be removed when CO_2 was used solely as the oxidizing gas, whereas more than 98% was removed then the oxidant gas comprised air. The use of pure CO_2 led to the formation of lanthanum carbonates, whereas the use of air led to the formation of the above described metal-organic nanocrystalline product.

1. An electrochemical process for recovering reaction products of a metal element or a metalloid element or a mixture of two or more thereof from at least one water soluble precursor compound comprising the metal element or the metalloid element or two or more thereof, in the form of nano particles, in particular nano crystals of at least one reaction product, wherein the process comprises:

supplying a solution of the water soluble precursor compound to a water-based catholyte of a cathode compartment of an electrochemical cell, equipped with a cathode comprising a gas diffusion electrode, wherein the gas diffusion electrode comprises a porous electrochemically active material having a BET surface area of at least 50 m^2/g,

adjusting the pH of the catholyte to a pH which is smaller than the pKa of the water soluble precursor compound,

supplying at least one oxidant gas to the gas diffusion electrode,

subjecting the cathode to an electrochemical potential to cause reduction of the at least one oxidant gas to one or more of the corresponding peroxide, ionic and/or radical reactive species capable of reacting with a cation comprising the metal element, or the metalloid element or the mixture of two or more thereof, to nano particles of the at least one reaction product with an average particle size, in particular nano crystals with an average crystallite size, equal to or smaller than 30.0 nm.

2. The process as claimed in claim **1**, wherein the at least one water soluble precursor compound comprises the metal element or the metalloid element in the form of a cation of the metal or the metalloid element, or the at least one water soluble precursor compound comprises a cation comprising the metal element or the metalloid element or the mixture of two or more thereof, or the at least one water soluble precursor compound comprises a mixture of two or more of the afore mentioned compounds.

3. The process as claimed in claim **1**, wherein the oxidant gas is an inorganic oxidant gas or a mixture of two or more of such gases.

4. The process as claimed in claim **3**, wherein the inorganic oxidant gas is selected from the group consisting of ozone, oxygen, carbon oxides, nitrogen oxides, halogen oxides, sulfur oxides, halogens, air, biogas, flue gas, acid gas, combustion exhaust gas, or a mixture of two or more of the afore mentioned gases or a mixture of two or more of the afore mentioned oxidant gases.

5. The process according to claim **1**, wherein a supply rate with which the oxidant gas is supplied to the gas diffusion electrode is variable.

6. The process according to claim **1**, wherein a partial pressure of the oxidant gas that is supplied to the gas diffusion electrode is variable.

7. The process as claimed in claim **1**, wherein the at least one water soluble precursor compound is supplied to the water-based catholyte as a solution of the water soluble precursor in water.

8. The process as claimed in claim **1**, wherein the at least one water soluble precursor compound is supplied to the water-based catholyte as a solid, and is at least partly dissolved in the catholyte.

9. The process as claimed in claim **1**, wherein a concentration of the at least one water soluble precursor compound supplied to the water-based catholyte is variable.

10. The process as claimed in claim **1**, wherein the catholyte has an ionic conductivity of at least 1.0 mS/cm.

11. The process as claimed in claim **1**, wherein the electrochemically active material comprises an active surface having at least one weak acid or weak basic functional group or a mixture of at least one weak acid and weak basic group.

12. The process as claimed in claim **1**, wherein a hydrophilic side of the electrochemically active surface of the gas diffusion electrode encompasses a plurality of functional groups which may be polarized or deprotonated upon application of the electrochemical potential.

13. The electrochemical process as claimed in claim **1**, wherein in advance of supplying the water soluble precursor compound to the cathode compartment, the pH of the catholyte is adjusted to a $pH \leq 7$, preferably to a $pH \leq 5$.

14. The electrochemical process as claimed in claim **1**, wherein an aqueous solution of a weak protonic electrolyte is supplied to the catholyte, preferably a weak protonic base or a weak protonic acid, more preferably a weak polyprotonic base or a weak polyprotonic acid.

15. The electrochemical process as claimed in claim **14**, wherein the weak protonic acid has a pKa which is at least one unit higher than the pH of the catholyte.

16. The electrochemical process as claimed in claim **14**, wherein the weak protonic base has a pKa of between 6.0 and 12.0, preferably between 7.0 and 11.0.

17. The electrochemical process as claimed in claim **1**, wherein the electrochemically active material has a BET surface area of at least 100 m^2/g, preferably at least 200 or 250 m^2/g, more preferably at least 400 or 500 m^2/g, most preferably larger than 750 or 1000 m^2/g.

18. The electrochemical process as claimed in claim **1**, wherein a binary electrolyte is supplied to the catholyte with the purpose of raising an electric conductivity of the catholyte, preferably raising an electric conductivity of the catholyte to at least 5 $mS\cdot cm^{-1}$, more preferably between 20 and 80 $mS\cdot cm^{-1}$, most preferably between 20 and 50 $mS\cdot cm^{-1}$.

19. The electrochemical process as claimed in claim **18**, wherein the binary electrolyte is a water soluble ionic salt or a mixture of two or more of such salts, but preferably the binary electrolyte is sodium chloride,

20. The electrochemical process as claimed in claim **1**, wherein an ionic liquid is supplied to the catholyte, in a molar ratio of at least 10:1 with respect to the water soluble precursor compound, with the purpose of producing nanocrystals containing the ionic liquid or one or more of its decomposition products.

21. The electrochemical process as claimed in claim **20**, wherein the ionic liquid is a hydrophilic ionic liquid, preferably tetrabutylammonium chloride or tetrabutyl ammonium bromide.

22. The electrochemical process as claimed in claim **1**, wherein the electrochemical potential to which the cathode is subjected is a reducing potential relative to a reference electrode, which is below the thermodynamic pH potential equilibrium region of stability of the oxidant gas in water, preferably below the region of thermodynamic stability of water, more preferably outside of the region of thermodynamic stability of hydrogen.

23. The electrochemical process as claimed in claim **1**, wherein the precursor compound is a compound of an ion of an element selected from the group consisting of group I, II, III and IV elements of the periodic table of elements, transition metal elements, actinides and lanthanides and a compound containing two or more of such elements.

24. The electrochemical process as claimed in claim **1**, wherein the electrochemical potential to which the cathode is subjected is reversed with the purpose of recovering the nano crystals from an electrochemical active porous material at the gas-diffusion cathode.

25. The electrochemical process as claimed in claim **1**, wherein one or more additives are supplied to the catholyte, the one or more additives being selected from the group consisting of dispersants, stabilizers, surfactants, polymers, copolymers, emulsifiers, cross-linking agents, capping agents and free flow agents and a mixture of two or more of these compounds.

26-31. (canceled)

32. A method for selectively isolating a reaction product of at least one metal element or a metalloid element or two or more thereof from an aqueous solution comprising a water soluble precursor compound thereof, wherein use is made of the process as claimed in claim **1**.

33. (canceled)

34. The process as claimed in claim **1**, wherein the electrochemically active material comprises at least one weak protonic acid or weak protonic basic functional group or a mixture of at least one weak protonic acid and weak protonic basic group.

35. The process as claimed in claim **12**, wherein the functional groups contain one or more moieties selected from the group consisting of a nitrogen containing moiety, an oxygen containing moiety, a chlorine containing moiety and a sulfur containing moiety.

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