



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
17.03.2021 Bulletin 2021/11

(51) Int Cl.:
C25B 1/21 (2006.01)

(21) Application number: **19020520.3**

(22) Date of filing: **10.09.2019**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(72) Inventors:
• **Patro, Modestino Rafael Alberto**
2400 Mol (BE)
• **Dominguez-Benetton, Xochitl**
2400 Mol (BE)
• **Elisabet, Andres Garcia**
2400 Mol (BE)
• **Fransaer, Jan**
3000 Leuven (BE)

(71) Applicants:
• **VITO NV**
2400 Mol (BE)
• **Katholieke Universiteit Leuven, K.U.Leuven R&D**
Leuven 3000 (BE)

(74) Representative: **Luys, Marie-José A.H.**
Vito N.V.
Boeretang 200
2400 Mol (BE)

(54) **A PROCESS FOR PRODUCING MIXED METAL OXIDES AND HYDROXIDES**

(57) An electrochemical process for producing crystalline nanoparticles of a mixed metal oxide, mixed metal hydroxide or mixed metal oxide hydroxide reaction product containing at least a first and a second metal ion which are different from each other, the method comprising the steps of

- (1) supplying to a cathode compartment of an electrochemical cell equipped with a gas diffusion cathode, a liquid feed electrolyte solution containing a first precursor salt of the first metal ion in a first concentration and a second precursor salt of the second metal ion in a second concentration to obtain a reaction mixture;
- (2) supplying an O₂ containing oxidant gas to the cathode,
- (3) subjecting the cathode to an electrochemical potential

which is below the thermodynamic limit of O₂ reduction at the pH of the reaction mixture,

- (4) applying a potential to the electrode to cause reduction of the O₂ contained in the oxidant gas to one or more of the corresponding peroxide, OH⁻, ionic and/or radical reactive O containing species,
- (5) wherein a ratio R_Q of charge Q applied to the cathode relative to the sum of the individual concentrations of the at least one first and second metal ion ([M₁] + [M₂]) ranges between 100 and 1500 C/mmol, wherein [M₁] is the concentration of the first metal ion in the reaction mixture and [M₂] is the concentration of the second metal ion in the reaction mixture, and isolating nanoparticles of the reaction product.

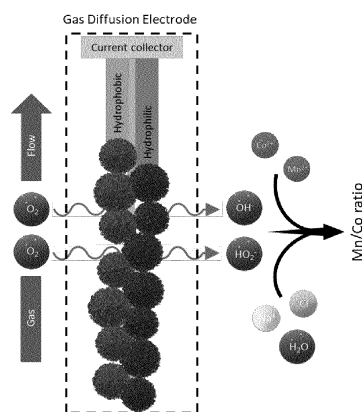


Figure 1a

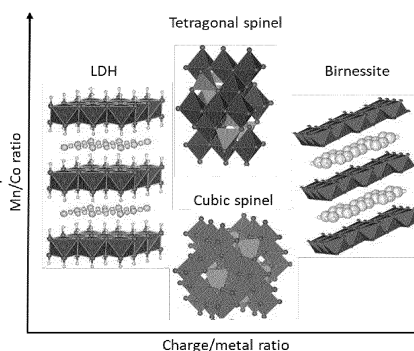


Figure 1b

Description

[0001] The present invention relates to an electrochemical process for producing crystalline nanoparticles of a mixed metal oxide, mixed metal hydroxide or mixed metal oxide hydroxide reaction product containing at least a first and a second metal ion which are different from each other, the structure of which may either be layered, a cubic or tetragonal spinel or a birnessite by tuning the process parameters, according to the preamble of the first claim.

[0002] Mixed metal oxides (hereafter referred to as MMOs) or hydroxides (hereafter referred to as MMHs) both of them hereafter referred to as MMX are a family of single-phase metal oxides or hydroxides which contain two or more kinds of metal cations. The complex chemical composition, interfacial characteristics and synergistic effects caused by the presence of multiple metal species, provide these materials with superior and special properties when compared to simple metal oxides comprising a single kind of metal cation [Wu, Bai, Feng, Xiong. Porous mixed metal oxides: design, formation mechanism, and application in lithium-ion batteries. *Nanoscale* 2015,7(41), 17211-17230]. Structural groups embodying MMX include spinels (SPIN), birnessites (BIR), layered double hydroxides (LDH), perovskites (PVK), and garnets (GRT), among others.

[0003] A specific type of manganese dioxide, δ -MnO₂, forms birnessite (BIR) and birnessite-type compounds. Birnessite-type compounds are layered oxides, composed of Mn-O octahedra plates with intercalated water. The redox activity of Mn allows part of the metal in the oxide layers to deviate from a 4⁺ valence to 3⁺. Electroneutrality is conserved by the presence of intercalating small cations, usually Mg²⁺, Li⁺, Na⁺, K⁺, etc. [Johnson, E. A. & Post, J. E., Water in the interlayer region of birnessite: Importance in cation exchange and structural stability. *American Mineralogist* 91, 609-618 (2006)]. This makes birnessite-type MnO₂ a natural candidate cathode material for alkali and alkali-earth batteries, as well as supercapacitors and electrocatalysts (ORR/OER) [Nam, K. W. et al. The high performance of crystal water containing manganese birnessite cathodes for magnesium batteries. *Nano letters* 15, 4071-4079 (2015)].

[0004] Another family of materials that has jumped to the forefront of research on supercapacitors, is the one of layered double hydroxides (LDHs). LDHs are inorganic ionic solids, characterized by a lamellar structure with the generic layer sequence [AcB Z AcB]_n, where c represents layers of metal cations, A and B are layers of hydroxide anions, and Z are layers of other anions and neutral molecules, such as water. The intercalated anions Z are weakly bound, often exchangeable; their intercalation properties have scientific and commercial interest. The potential of these LDHs as electrode materials arises from their high redox activity, their high ion intercalation capacity and high specific capacitance. The design of LDHs both in terms of the intercalated ion and metal hydroxide composition, permits targeting specific properties which confer them unique synthetic identities. This is an area to be exploited in order to fully realize the potential of these materials [Xie, L. et al. Co x Ni 1- x double hydroxide nanoparticles with ultrahigh specific capacitances as supercapacitor electrode materials. *Electrochimica Acta* 78, 205-211 (2012)].

[0005] Spinel is an inorganic solid of general formulation AB₂X₄, wherein X correspond to anions (typically chalcogens, like oxygen), arranged in a cubic close-packed lattice, and A and B correspond to cations, occupying some or all of the octahedral and tetrahedral sites in the lattice, of a cubic (isometric) crystal system. The charges of A and B in prototypical spinel structures are +2 and +3, respectively (A²⁺B³⁺2X₂₋₄). Other combinations incorporating divalent, trivalent, or tetravalent cations, including Mg, Zn, Fe, Mn, Al, Cr, Ti, and Si, are possible. In another type of material A and B can be the same metal with different valences, as is the case with magnetite Fe₃O₄ (Fe²⁺Fe³⁺₂O₂₋₄). Both birnessites and LDHs are excellent precursors for the synthesis of spinels, since they allow for a virtually uniform distribution of the cations. This is a useful feature when the synthesis of compounds with complex stoichiometries is intended. An uneven distribution of metals is a frequently occurring problem in solid state synthesis, which is the method commonly employed for the production of complex spinels.

[0006] Mixed Mn-Co oxides and hydroxides with a vast number of possible chemical compositions exist. Regardless of the precursors, spinels of the general formula Mn_{3-x}Co_xO₄ are found in numerous applications, including batteries, fuel cells, and (electro)catalysis [Cheng, F. et al. Rapid room-temperature synthesis of nanocrystalline spinels as oxygen reduction and evolution electrocatalysts. *Nature chemistry* 3, 79 (2011); Zhou, L., Zhao, D. & Lou, X. W. Double-shelled CoMn₂O₄ hollow microcubes as high-capacity anodes for lithium-ion batteries. *Advanced Materials* 24, 745-748 (2012)]. Efforts to steer away from solid-state techniques include synthesis of various Mn-Co-based materials by chemical precipitation [Zhou, L., Zhao, D. & Lou, X. W. Double-shelled CoMn₂O₄ hollow microcubes as high-capacity anodes for lithium-ion batteries. *Advanced Materials* 24, 745-748 (2012)], by hydrothermal methods [Liang, Y. et al. Covalent hybrid of spinel manganese-cobalt oxide and graphene as advanced oxygen reduction electrocatalysts. *Journal of the American Chemical Society* 134, 3517-3523 (2012)] and sol-gel methods [Lavela, P., Tirado, J. & Vidal-Abarca, C. Sol-gel preparation of cobalt manganese mixed oxides for their use as electrode materials in lithium cells. *Electrochimica Acta* 52, 7986-7995 (2007)]. Particularly in the case of spinels, which are traditionally synthesized at high temperatures, these approaches yield particles which are crystalline, but often large and irregular [Li, C. et al. Phase and composition controllable synthesis of cobalt manganese spinel nanoparticles towards efficient oxygen electrocatalysis. *Nature communications* 6, 7345 (2015)]. Recent efforts attempted to develop synthesis routes for the production of spinels at room temperature [Cheng, F. et al. Rapid room-temperature synthesis of nanocrystalline spinels as oxygen reduction and

evolution electrocatalysts. Nature chemistry 3, 79 (2011)], birnessites [Kai, K. et al. Room-temperature synthesis of manganese oxide monosheets. Journal of the American Chemical Society 130, 15938-15943 (2008)] and layered double hydroxides (LDHs) [Song, F. & Hu, X. Ultrathin cobalt-manganese layered double hydroxide is an efficient oxygen evolution catalyst. Journal of the American Chemical Society 136, 16481-16484 (2014)]. Common to these synthesis techniques is the need to use several Co-Mn precursors, oxidants, or reductants, to achieve the desired structure. The large spread of the electrochemical performance of these materials reported in literature emphasizes the lack of control and reproducibility when synthesizing these, especially in terms of microstructure [Katsounaros, I., Cherevko, S., Zerad-janin, A. R. & Mayrhofer, K. J. Oxygen electrochemistry as a cornerstone for sustainable energy conversion. Angewandte Chemie International Edition 53, 102-121 (2014)].

[0007] Amongst others, composition, crystallinity and morphology define a synthetic identity and are key factors in structure-property relations for any given structure of Mn-Co oxides [Cheng, F. & Chen, J. Metal-air batteries: from oxygen reduction electrochemistry to cathode catalysts. Chemical Society Reviews 41, 2172-2192 (2012)]. From literature data it appears that the properties obtained are closely related to the synthesis process.

[0008] There is therefore a need to a synthesis method with which mixed metal oxides, mixed metal hydroxides or mixed metal oxide hydroxide materials may be produced, which permits to tune the chemical composition and structure of the end product. This would provide a valuable platform for future screening of materials. However, it does not exist up to now.

[0009] CN102976373A discloses a method for synthesizing monodisperse stable layered double hydroxides as colloid nanocrystalline, comprising the steps of

- milling of a NaOH solution and two metal ion precursors (i.e., Mg^{2+} and Al^{3+} precursors) to obtain a slurry,
- centrifugally washing the slurry and transferring it to a hydrothermal kettle to recrystallize and obtain a stable colloid solution.

The colloid solution is added to several density gradient medium solutions with different densities and subjected to centrifuging. Colloid nano particles with different sizes have different sedimentation rates in the density gradient solutions, and will accumulate in the gradient solutions with the corresponding density. The method disclosed in CN102976373 relies on adjusting the molar ratio of the metal precursors, i.e., Mg^{2+}/Al^{3+} in a ratio between 1.5 to 3, to obtain an end product with a desired particle size distribution and the incorporation in the process of a separation step to separate nano particles of different sizes. The process does however not permit to tune the chemical composition and structure of the end product.

[0010] KR101415729B1 discloses a method for manufacturing layered double hydroxides using co-precipitation of hydroxide ions and anionic quantum dot nanoparticles, that react with a metal cation solution. The metal cation solution includes both a divalent metal ion and a trivalent metal ion, besides gadolinium ions. The anionic quantum dot nanoparticles are inserted between the layers of the LDH. The method however leads to a large dispersity in particle size and varying material properties (e.g. valence state, lattice parameter, crystallite size). Besides this, temperatures as high as 300°C are used, hazardous solvents are employed as well as hazardous chemicals as "surface coupler", such as bromide, epoxy, thiol, vinyl, polysulfides, isocyanate, nitroso, etc.,. The process is slow and although it is implied that control over properties is reached, it is not clear which technical features are controlled achieve such control.

[0011] WO2012150460 discloses a method for the preparation of layered double hydroxides as particles having a rod-like morphology, by contacting hydrothermally produced rod-like aluminium hydroxide precursor particles with an aqueous lithium salt. The hydrothermal treatment however involves the use of high temperatures typically 130 to 250 °C, and although it typically produces crystalline particle sizes, the particle sizes are usually large.

[0012] EP3242963B1 discloses an electrochemical process for recovering metal or metalloid compounds from a water soluble precursor thereof in the form of nano crystals. The process comprises the steps of :

- supplying a solution of the water soluble precursor compound to the cathode compartment of an electrochemical cell,
- 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 or metalloid element or a mixture thereof, so that nano particles are formed with an average particle size of maximum 30.0 nm.

The process disclosed in EP3242963-B1 does however not permit to tune both the chemical composition and structure of the end product, i.e. it does not disclose how the process may be tuned to either produce a layered material or a material with a cubic spinel crystal structure.

[0013] There is thus a need to a method with which crystalline nanoparticles may be produced of a mixed metal oxide,

mixed metal hydroxide or mixed metal oxide hydroxide reaction product, which contain at least a first and a second metal ion which are different from each other, wherein the reaction product has a desired crystalline structure selected from a wide variety of crystalline structures and a desired stoichiometric composition selected from a range of possible stoichiometric compositions.

[0014] The present invention therefore seeks to provide a method for producing crystalline nanoparticles of a mixed metal oxide, mixed metal hydroxide or mixed metal oxide hydroxide reaction product, which contain at least a first and a second metal ion which are different from each other, wherein the reaction product has a desired crystalline structure selected from a wide variety of crystalline structures and a desired stoichiometric composition selected from a range of possible stoichiometric compositions.

[0015] This is achieved according to the present invention with a method which shows the technical features of the characterizing portion of the first claim.

[0016] Thereto, the present invention relates to an electrochemical process for producing crystalline nanoparticles of a mixed metal oxide, mixed metal hydroxide or mixed metal oxide hydroxide reaction product containing at least a first and a second metal ion which are different from each other, the method comprising the steps of

(1) supplying to a cathode compartment of an electrochemical cell equipped with a gas diffusion cathode, a liquid feed electrolyte solution containing a first precursor salt of the first metal ion in a first concentration and a second precursor salt of the second metal ion in a second concentration to obtain a reaction mixture;

(2) supplying an O₂ containing oxidant gas to the cathode,

(3) subjecting the cathode to an electrochemical potential which is below the thermodynamic limit of O₂ reduction at the pH of the reaction mixture,

(4) applying a potential to the electrode to cause reduction of the O₂ contained in the oxidant gas to one or more of the corresponding peroxide, OH⁻, ionic and/or radical reactive O containing species,

(5) wherein a ratio R_Q of charge Q applied to the cathode, relative to the sum of the individual concentrations of the at least one first and second metal ion ([M₁] + [M₂]) ranges between 100 and 1500 C/mmol, wherein [M₁] is the concentration of the first metal ion in the reaction mixture and [M₂] is the concentration of the second metal ion in the reaction mixture,

(6) and isolating nanoparticles of the reaction product.

[0017] In a preferred embodiment, R_Q ranges between 125 and 1250 C/mmol, more preferably between 150 and 1000 C/mmol.

[0018] The inventors have observed that by adapting or tuning the reaction conditions, a.o. the charge applied, the total metal ion concentration and the relative concentration of the different metal ions present in the feed solution, in such a way that R_Q falls within the indicated ranges, crystalline nanoparticles of mixed metal oxide, mixed metal hydroxide or mixed metal oxide hydroxide reaction products may be produced, with a desired stoichiometry, crystal structure, crystallite size and lattice parameters. Contrary to the prior methods, the present invention does not inevitably lead to a limited range of products as the vast majority of processes does.

[0019] Additionally, by tuning the reaction conditions, in particular the oxygen flow rate and anode potential, formation of desired oxygen vacancies may be controlled, which in turn may cause certain desired defects to be formed in the crystal structure of the reaction product. This is important as the crystal structure, stoichiometry, lattice parameters, crystallite size, defects and oxygen vacancies, may confer desired properties to the reaction product, such as magnetic properties, catalytic activity, the spacing between layers and nature of the ions present between adjacent layers.

[0020] The inventors have further found that by varying R_Q within the indicated range, both the degree of oxidation of the metal ions, the average oxidation state of each of the metal ions in the reaction product may be controlled as well as the crystal structure of the reaction product. In particular by varying R_Q within the indicated range, nano particles having either a double layered structure, a cubic spinel crystalline structure or a tetragonal crystalline structure may be formed. Thereby, the higher R_Q, the higher the average oxidation state of the metal ions in the end product may be.

[0021] Varying the charge applied permits controlling the oxidation state of the metal and/or metalloid ions in the reaction product.

[0022] At constant charge applied, the nature, i.e. the chemical composition of the reaction product may be adapted or controlled by varying the feed solution supply rate or the concentration of the precursor salts contained therein and the relative concentration of the metal ions contained therein. Or else at constant feed solution supply rate, concentration and composition, the nature of the reaction product may be adapted or controlled by varying the charge applied.

[0023] The method of the present invention is suitable for use with a wide variety of metal ions. In fact, the method of this invention may be used with every metal ion capable of forming an oxide or a hydroxide. Therefore, the first and second metal ion may independently of each other be selected from the elements of Group I, Group II, Group III, the transition metals and the lanthanides of the Periodic System of the Elements. Preferably however, the first and second metal ion may independently of each other be selected from Group I, Group II, Group III, the transition metals, more

preferably from Li, Al, Co, Mn, Ni, Fe, Zn, Cu, one or more of the Pt group metals, or a mixture containing two or more hereof.

[0024] An example of a group of reaction products includes those which range from MnO_2 to $\text{Mn}(\text{OH})_2$, which result from opposite extreme values of R_Q and mainly comprise layered materials. Reaction conditions may however also be controlled in such a way that intermediate oxidation states of Mn are formed, which mainly lead to the formation of spinels. Another example of a reaction product that may be produced with the method of this invention includes $\text{Co}_{1-y}\text{Mn}_y(\text{OH})_2\text{Cl}_y$ with a LDH structure.

[0025] The method of the present invention may be carried out in one single electrochemical cell, in such a way that there is no need of transferring intermediate reaction products from one reactor to another to subject them to specific conditions.

[0026] In a preferred embodiment, the cathode is a gas diffusion electrode provided with a porous electrochemically active material. The inventors have observed that conventional electrodes favour formation of films or sheets of the end product, whereas the use of a gas diffusion electrode permits producing a particulate material with a desired particle size.

[0027] The method of this invention is suitable for being carried out in a batchwise manner. However, by arranging for a continuous flow of feed solution and a continuous recovering of the reaction product particles, the method of this invention may also be carried out as a continuous process.

[0028] The method of this invention will generally be carried out with liquid catholytes and liquid feed solutions.

[0029] Preferred embodiments of this invention relate to mixed oxide and/or mixed hydroxide reaction products in which the at least one first and second metal ions may either be ions of different metals or ions of a same metal having a different oxidation state, or a combination hereof.

[0030] Varying the ration of the concentration of the metal or metalloid ions in the feed solution permits to control and to vary the chemical composition of the reaction product. Reaction products may for example range from MnO_2 to $\text{Mn}(\text{OH})_2$. Reaction conditions may however also be controlled in such a way that intermediate oxidation states of Mn are formed.

[0031] According to a preferred embodiment of the invention a ratio of the concentration of the at least one first and second metal ion to the total metal ion concentration in the feed solution, i.e. $X_{Mi} = [M_i] / \sum [M_n]$, with n being the number of different metal ions in the feed solution, may be varied. In particular, the ratio of the concentration of the first metal ion to the total metal ion concentration in the feed solution, i.e. $X_{M1} = [M_1] / \sum [M_n]$ may be varied. Similarly, the ratio of the concentration of the second metal ion i.e. X_{M2} and any further metal ion i.e. X_{Mi} , to the total metal ion concentration in the feed solution may be varied. Depending on the nature of the metal ion and the ratio selected, the average valence of the metal ions in the reaction product, the stoichiometry and crystal structure of the reaction product may be varied and controlled. $X_{M1} = [M_1] / \sum [M_n]$ may vary within wide ranges, depending on the stoichiometry of the envisaged reaction product and the average valence of the metal ions present therein. In particular for each metal ion X_{Mi} may vary from 0 to 1. With different metal ions is meant ions of different metals as well as ions of the same metal having a different valency.

[0032] In a preferred embodiment of this invention the total metal ion concentration present in the feed solution ranges between 0.1 mM and 15mM. Preferably the total metal ion concentration present in the feed solution that is supplied to the cathode compartment ranges between 0.15 mM and 15mM, more preferably between 1 mM and 10 mM, most preferably between 1 mM and 7mM. The total metal ion concentration in the reaction mixture may be varied, not only by varying the metal ion concentration.

[0033] However, when use is made of electrodes with a large surface area, metal ion concentrations may be increased. In fact the total metal ion concentration in the feed solution which gives rise to the formation of the desired reaction product, depends on the dimensions, i.e. active surface area of the cathode. The person skilled in the art will be capable of adapting the total metal ion concentration to the cathode surface area in order to obtain the desired reaction product.

[0034] By varying the metal ion concentration in the reaction medium, the average valence of the metal ions in the reaction product and the stoichiometry of the reaction product may be varied. Preferably the concentration of the precursor metal ions is as high as possible as this provides a reaction front with a high concentration of reactive species which is expected to lead to the formation of metal particles at the reaction front itself, whereas a low concentration of precursor metal ions is expected to permit moving of the precursor metal ions towards the electrode and to result in a reaction product in the form of a film.

[0035] The inventors have observed that above a maximum concentration the risk increases to the occurrence of left over metal ions in the electrolyte due to insufficient charge to permit precipitation. Structural strain may increase and result in crystal structure distortions, which may ultimately lead to the formation of a different crystalline phase. With increasing metal ion concentrations the risk to clogging of the electrode/cathode increases and the charge applied to the cathode must be increased if full conversion of the metal ions contained in the feed solution is envisaged. Further, the risk increases that a mixture of desired reaction products and unwanted side products is obtained and/or that the reaction conditions shift towards a window wherein a different reaction product is obtained, than the one that was intended.

[0036] In order to be able to control the reaction rate, i.e. the rate with which the end products are formed, the electrolyte flow rate into the cathode chamber may be varied. Within the scope of this invention, the rate with which the electrolyte is supplied to the cathode chamber with a flow rate of between 1 and 150 ml/min, preferably between 5 and 100 ml/min,

more preferably between 5 and 50 ml/min.

[0037] By varying the electrolyte flow rate, the particle size of the mixed oxides and/or mixed hydroxides may be varied, faster flow rates giving rise to smaller particle sizes.

[0038] The electrolyte flow rate will generally determine the residence time of the reactants in the electrochemical cell. The electrolyte flow rate may also influence the pH at the outlet of the electrochemical cell, as the pH in turn is influenced by the residence time of the reactants in the electrochemical cell. The inventors have observed that by varying the electrolyte flow rate, cation oxidation rates may be varied and give rise to reaction products with a varying crystal structure, varying average metal ion valence and a varying stoichiometry.

[0039] The flow rate with which the O₂ containing oxidant gas may be supplied to the cathode is preferably variable. In a preferred embodiment a supply rate with which the oxidant gas is supplied to the gas diffusion electrode ranges between 5.0 and 300.0 ml/min, preferably between 5.0 and 250.0 ml/min, more preferably between 5.0 and 150.0 ml/min. Without wanting to be bound by this theory, it is assumed that within in these ranges a sufficiently high concentration of the oxidant gas in the gas diffusion electrode exists to achieve a desired degree of oxidation of the metal ions and obtain a reaction product with a desired crystal structure and stoichiometry. In particular it is assumed that the oxidant gas is capable of penetrating the gas diffusion electrode and is thereby available to participate in the oxidation of the metal ions as is described below.

[0040] At higher flow rates the risk increases that penetration of the oxidant gas into the gas diffusion electrode diminishes and lead to incomplete oxidation of the reactive species or that mechanic disruption of the gas diffusion electrode occurs. In general, the oxidant gas flow rate may be adapted such that an overpressure at the gas diffusion electrode is created which is sufficiently high so that sufficient oxidant gas is available and sufficiently low to minimize the risk to mechanic disruption of the electrode. Therefore, the oxidant gas flow may be controlled so that the overpressure at the gas diffusion electrode varies between 5 and 30 mbar.

[0041] The oxidant gas used in the process of this invention may consist of pure O₂ or a mixture of O₂ with one or more other gases, which are preferably inert to the electrochemical reaction. Examples of such inert gases include N₂, or a noble gas, more particularly Ar. When using a mixture of gases (e.g., O₂ and N₂) the skilled person will be capable of adjusting the molar fraction of the oxidant gas in such a way that it is sufficiently high to enable its electrochemical reduction, as low oxygen molar fractions may limit the extent of reaction due to production of O₂ containing species with low reactivity or not enough of them to reach the conditions to form the nanocrystals intended. Thereby, preferably the O₂ mole fraction in the O₂ containing oxidant gas is at least 0.05, more preferably at least 0.10, most preferably at least 0.15, although the O₂ mole fraction in the O₂ containing oxidant gas may be as high as 1. As O₂ is an essential element of the oxidation process and a source for OH⁻ production, varying the O₂ mole fraction in the oxygen containing oxidant gas will permit to control the stoichiometry of the end product.

[0042] In a preferred embodiment, wherein the O₂ mole fraction in the oxidant gas ranges between 0.05 and 1.0, preferably between 0.05 and 0.75, more preferably between 0.10 and 0.30.

[0043] In order to have a sufficiently high concentration of the oxidant gas at the active electrode surface, an over pressure is maintained in in the cathode compartment, preferably an overpressure of at least 5 mbar. According to a different preferred embodiment an overpressure may be maintained of between 1 and 500 mBar, preferably between 1 and 250 mBar, more preferably between 1 and 100 mBar, most preferably between 2.5 and 50 mBar, in particular between 5 and 30 mBar. This is done to force the oxygen to flow through the gas diffusion electrode instead of flowing along and escaping the electrochemical reactor.

[0044] The method of this invention may be carried out in a water based catholyte which only contains water as the liquid phase or water in combination with one or more organic solvents. Although the use of water is preferred in view of minimizing toxicity of the end product, the method of this invention may also be carried out in a catholyte which contains a mixture of water and one or more organic solvents, or in an aprotic organic solvent or a mixture of two or more aprotic organic solvents.

[0045] Preferred embodiments of this invention relate to a method wherein the electrolyte is a mixture of water and at will permit controlling the particle size of the mixed metal oxide and/or mixed metal hydroxide reaction products. In particular in case the mixed metal oxide and/or mixed metal hydroxide reaction products have a layered structure, an appropriate selection of the at least one organic solvent and its concentration in the electrolyte will permit to control the distance between the layers of the layered structure.

[0046] The skilled person will be capable of selecting the most appropriate solvent and the amount of solvent used, taking into account a.o. the solubility of the precursor salts, the ability of the end product to precipitate therein, the particle size and layer intercalation to be achieved and the envisaged application of the nanoparticles. An appropriate selection of the solvent and the concentration of the solvent in the catholyte will permit controlling the dimensions of the average particle size of the nanoparticles and their dispersibility. Therefore, water, a polar solvent or a mixture hereof may generally be used when the formation of larger nanoparticles is envisaged.

[0047] Organic solvents suitable for use in the method of this invention include dimethylformamide (DMF), dimethyl sulfoxide (DMSO), propylene carbonate, and acetonitrile, or their equivalents known to the skilled person. When use is

made of such organic solvents, to ensure a sufficient conductivity, the solvent may contain a supporting electrolyte, for example tetrabutylammonium chloride (TBAC), or tetrabutylammonium bromide (TBAB).

[0048] In case the production is envisaged of layered structure comprising intercalating anions or cations between the layers, a supporting electrolyte may be supplied to the reaction mixture to intervene in several aspects in the process of this invention. The inventors have observed that depending on the nature of the reaction product, cations or anions of the supporting electrolyte may intercalate between the layers of the reaction produced with the method of this invention.

[0049] Supporting electrolytes suitable for use with this invention are generally known to the skilled person and they include aqueous solutions of one or more soluble salts, for example soluble salts of alkali metal ions, earth alkali metal ions, in particular Na, K or Mg salts, but many other salts may be used as well. The cations will be capable of intercalating between the layers of a mixed oxide in case a mixed oxide is formed. The anion of the supporting electrolyte may vary and suitable anions include halogenides, carbonates, sulfates, nitrates, perchlorates or phosphates, or any other suitable anion, and mixtures of the afore mentions supporting electrolytes may be used as well. The anions will be capable of intercalating between the layers of the mixed hydroxides, in case a mixed hydroxide is formed. The skilled person will be capable of selecting the appropriate supporting electrolyte depending on the nature of the desired intercalating cations and anions.

[0050] The presence of the supporting electrolyte will contribute to maintain the ionic conductivity of the catholyte at a sufficiently high level in the course of the reaction, to have the electrochemical conversion proceeding sufficiently fast. A supporting electrolyte may also intervene in controlling the average size of the nano particles of the reaction product, and may ensure that the average particle size is maintained within the desired ranges and that particle aggregation may be controlled. Increasing amounts of supporting electrolyte will generally permit limiting the average particle size and limiting aggregation to larger particles to a desired extent.

[0051] To that end, preferably use is made of a catholyte with and an ionic conductivity of at least 1.0 mS/cm, preferably at least 10 mS/cm. Maintaining of the conductivity at a sufficiently high level may be of particular importance when the process of this invention is operated in a continuous manner, and continuous supply of precursor salts and withdrawal of end product takes place. By the presence of the supporting electrolyte, the conductivity of the catholyte may be increased to at least 5 mS.cm⁻¹, more preferably between 20 and 80 mS.cm⁻¹ and even more preferably between 20 and 50 mS.cm⁻¹ and the risk to a varying conductivity in the course of the process may be minimised.

[0052] The supporting electrolyte is preferably supplied in a concentration of between 5.0 and 150.0 g/l of catholyte, preferably between 10.0 and 100 g/l, more preferably between 10.0 and 50.0 g/l. The presence of the supporting electrolyte will permit to control variations in the conductivity of the reaction mixture as a result of the conversion of the reactant precursor salts into the desired end product, and therewith limit the risk to slowing down of the reaction or the formation of end products with an unwanted stoichiometry. The use of these concentrations of supporting electrolyte will in general result in a catholyte with and an ionic conductivity of at least 1.0 mS/cm, preferably at least 10 mS/cm.

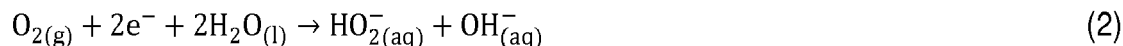
[0053] In the method of this invention, at the start of the reaction, the pH of the catholyte is preferably adjusted to a value between 2.0 and 6.0, preferably between 2.0 and 5.0, more preferably between 2.5 and 3.5 to achieve a sufficiently high yield of precipitated particles. The skilled person will be capable of adjusting the pH at the start of the reaction in such a way that the pH in the course of the reaction may rise to a sufficiently high level to promote precipitation of the desired reaction products.

[0054] The inventors have found that the pH at the start of the reaction may be varied taking into account the nature of the metal or metalloid ion contained in the precursor, to ensure that the precursor compound is dissolved in the reaction medium. Therefore, in an initial stage of the reaction, preferably the pH is adjusted in the acidic region, and preferably the initial pH of the reaction mixture is adjusted to 2.0 to ensure dissolution of the precursor compounds to the best possible extent.

[0055] As the reaction proceeds, the pH is preferably left to evolve, to ensure that precipitation of the metal oxide/hydroxide reaction products may precipitate. Although it is preferred to not add a pH buffering agent to the reaction mixture, in cases where it is envisaged to control the stoichiometry towards a desired direction a buffering agent may be supplied to the reaction mixture.

[0056] If so desired, to keep the pH within the desired limits as described above, an amount of a weak protonic electrolyte may be supplied to the catholyte. 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. 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 minimize the risk to the occurrence of unwanted side reactions. Within the indicated pH ranges, the pH is smaller than the pH range within which a relative predominance exists of the precursor salts in the ionic form. Within the indicated pH ranges, the pH is namely smaller than the pKa of the precursor salts.

[0057] Without wanting to be bound by this theory, the inventors believe that the oxygen present in the oxidant gas, is electrochemically reduced at the active porous carbon layer of the gas-diffusion cathode to form a.o. OH⁻ as follows :



[0058] The products obtained by the reduction of oxygen, profusely available at the electrochemical interface, react with the metals ions in solution, which are transported to the porous cathode material, via the electrolyte. When these metal ions meet the oxygen reduction reaction products or the highly reactive intermediaries, supersaturation is reached, which in turn leads to nucleation of e.g., hydroxides or oxides. Additive OH^- concentration and supersaturation keep ongoing, thus secondary nucleation and crystal growth proceed during the transient period of residence of the primary nuclei formed within the cathodic interface.

[0059] In order to ensure a sufficiently high reaction rate, the current density applied to the gas diffusion electrode ranges between 10 and 1000 Am^{-2} , preferably between 10 and 500 Am^{-2} , more preferably between 25 and 250 Am^{-2} . The current density namely determines the rate with which O_2 contained in the oxidant gas may be reduced to one or more of the corresponding peroxide, H_2O_2 , OH^- , ionic and/or radical reactive species. By controlling the current density, the crystal structure of the reaction product may be controlled and may be varied amongst the crystal structures shown in fig. 1. Low current densities will generally favour layered LDH crystals which correspond to generally less oxidized products, whereas high current densities will favour the formation of birnessite type reaction products which correspond to generally higher oxidized products and intermediate current densities will favour the formation of tetragonal or cubic spinel structures.

[0060] Controlling the electrolyte flow for a certain current density, or on the other hand controlling current density for a certain feed supply rate will permit controlling the crystal structure of the reaction product as described above.

[0061] In the process of this invention, usually the working potential of the cathode is set at a value between -50.0 and -750 mV vs. Ag/AgCl, preferably at a value between -100.0 and -650 mV, more preferably between -250 and -500 mV. An appropriate selection of the working potential will assist in obtaining an end product with a desired stoichiometry and nano particles with a desired average particle size. In general, more negative potentials approaching respectively -750 mV, - 650 mV or - 500mV are expected to increase the reaction rate. Potentials more negative than -750 mV could also lead to the product desired, however the hydrogen evolution reaction would be a competing process, reducing the current efficiency.

Gas diffusion electrode.

[0062] The electrochemically active material of the gas diffusion electrode which forms part of the cathode used in the process of this invention 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 have a high oxygen affinity and thus intervene in the oxidation of the metal ion or the metalloid ion.

[0063] 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.

[0064] Suitable porous material for use as the electrochemically active layer of the gas diffusion electrode 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 m^2/g , most preferably at least 400

or 500 m²/g, but those having a surface area larger than 750 or 1000 m²/g or even more may be particularly preferred. Porous materials particularly suitable for use as the electrochemically active layer include 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 m²/g, preferably at least 100 m²/g, more preferably at least 200 or 250 m²/g, most preferably at least 400 or 500 m²/g, but those having a surface area larger than 750 or 1000 m²/g or even more may be particularly preferred.

[0065] 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.

[0066] According to another preferred embodiment, the electrochemically active porous material is a solid which is dispersible or flowable in the water based electrolyte. Hereby, the solid may be made of one or more of the above described materials.

[0067] 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 be created at least in the cathodic gas compartment.

[0068] The method of this invention presents several advantages.

[0069] As has been explained above, the method of this invention does not inevitably lead to one single product or a limited range of products as the vast majority of processes does, but rather permits to produce mixed oxides and/or hydroxides with a desired geometric structure, a desired crystal structure, a desired stoichiometry, comprising the metal ions in a desired valence or valences (oxidation state ?), by an appropriate selection of the conditions in which the reaction is carried out. Reaction conditions that may be selected to control the reaction product as described above include, the initial pH of the reaction mixture, the precursor concentration in the feed solution, the oxidant gas partial pressure and flow rate, the feed solution flow rate etc. For example, by selecting the appropriate reaction conditions crystalline nano particles of a mixed oxide may be produced which may either take a layered structure, a cubic or a tetragonal spinel structure by varying the reaction conditions, or a LDH structure by varying the reaction conditions in a different way.

[0070] The present invention provides a process which is fast, with which crystalline nanoparticles of a mixed metal oxide, mixed metal hydroxide or mixed metal oxide hydroxide reaction product may be produced in one single reactor, using one single process step, wherein operational conditions may remain the same throughout the whole process and minimal adaptation is required (e.g., synthesis route, flow, temperature, potential, chemical environment, etc.).

[0071] This systematic approach to the synthesis of a variety of materials which is made possible by controlling the reaction conditions represents a valuable platform for future screening of materials. Such a platform did not exist up to now.

[0072] The present invention also relates to crystalline nanoparticles of a mixed metal oxide, mixed metal hydroxide or mixed metal oxide hydroxide reaction product containing at least a first and a second metal ion which are different from each other. As has been discussed above, this invention permits to produce metal or metalloid oxides or hydroxides or mixtures thereof which either are layered materials (LDH) layered double oxides or layered double hydroxides, show a cubic or tetragonal spinel crystal structure, by varying the reaction conditions as described above. The reaction products may be represented by the general formulas in the table below. Another type of reaction products that may be obtained with the method of this invention includes garnets which respond to the general formula $M^{2+}_3M^{3+}_2(SiO_4)_3$.

Crystal type	General formula	M1	M2	M3	A
spinel	$M_{2-3x}M_{3x}O_4$		M^{2+} cation e.g. Co^{2+} , Mn^{2+}	M^{3+} cation e.g. Mn^{3+} , Co^{3+}	
birnessite	$M_{1x}M_{2x}M_{3-1-x}O_2$	M^{+} cation, e.g. Na^{+} , Li^{+}	M^{3+} cation e.g. Mn^{3+} , Co^{3+}	M^{4+} cation, e.g. Mn^{4+}	
LDH type 1	$M_{2-1-x}M_{3x}(OH)_2A_x$		M^{2+} cation e.g. Co^{2+} , Mn^{2+}	M^{3+} cation e.g. Mn^{3+} , Co^{3+}	monovalent anion, e.g. Cl^{-} , Br^{-} , etc.
LDH type 2	$M_{1-2-2x}M_{3x}(OH)_2A_x$	M^{+} cation, e.g. Na^{+} , Li^{+}		M^{3+} cation e.g. Mn^{3+} , Co^{3+}	

[0073] The invention is further illustrated in the examples below.

[0074] The invention is further illustrated in the figures below and figure description.

[0075] Fig. 1a is a schematic representation of a gas diffusion electrode, Fig. 1b shows interactions occurring at the active surface of the gas diffusion electrode. Fig. 1c shows the crystal structures that may be produced with the present invention.

[0076] Fig. 2 shows pH profiles the 5 experiments described below with increasing initial metal concentration. From top to bottom: 1 mM, 2mM, 3 mM, 4 mM, and 5 mM. The bottom part of fig. 2 shows the evolution of the potential at the gas diffusion electrode upon starting the synthesis, with a current density of -30 Am.

[0077] Fig. 3 shows complex plane plots for the gas diffusion electrode in NaCl solutions at an influx pH of 3.5 with varying potential, gas choice and electrolyte concentration.

a) Effect of applied potential: 0.5 M NaCl, air, applied potentials as shown by the corresponding markers in the voltammetry. Inset: cyclic voltammetry taken at 10 mV s⁻¹.

b) Effect of oxygen concentration: 0.5 M NaCl, E = - 0.47 V, air (filled circles) and oxygen (empty circles) used in the gas chamber.

c) Effect of concentration of conducting electrolyte (NaCl): air, E = - 0.47 V, 0.5 M NaCl (filled circles) and 0.25 M NaCl (empty triangles).

[0078] Fig. 4 shows the phase diagram of the oxides and hydroxides resulting from the specified synthesis conditions, with a current density of -30 mA cm⁻². Each colored region is representative of the annotated phase, with transitions between resulting in phase mixtures. Center: XRD traces of 6 samples. From top to bottom: single-phase BIR, mix of BIR with CSPIN (CBIR), single-phase CSPIN, single-phase TSPIN, mix of TSPIN with LDH (TLDH), single phase LDH. The markers show the most prominent peak positions of BIR, CSPIN, TSPIN and LDH phases respectively.

[0079] Fig. 5 shows XRD traces of layered materials. Four birnessites with increasing amounts of cobalt, 3 layered double hydroxide, and a sample of a two-phase mixture of cobalt hydroxides. The basal spacing of the materials is shown in the inset.

[0080] Fig. 6 shows XRD traces of spinel materials. Cubic spinel (red) with increasing amounts of cobalt transitions into the tetragonal form (purple) with formula Co_xMn_{3-x}O₄. (Bottom left) Particle size measurements from SEM images of the boundary compositions is shown. (Bottom right) lattice parameters and crystallite sizes as a function of Co content.

[0081] Fig. 7 shows Oxygen Evolution Reaction catalysis evaluation for one selected material from each of the 4 structures examined. a) Linear Scan Voltammetry sweeps at 5 mV s⁻¹ in 1 M KOH solutions for the four structures. b) Tafel plots of the same LSV data with the slopes in the range of 1 mA cm⁻² to 10 mA cm⁻² annotated.

Examples.

[0082] The electrochemical reaction was carried out using an EC Micro Flow Cell electrochemical cell (ElectroCell, MFC30009) equipped with a DSA counter electrode. The reactions occurring at the electrode are schematically illustrated in figure 1a and 9.

[0083] A gas diffusion electrode (GDE) (VITO CORE®) is used as the cathode, the metal frame of the cathode compartment acts as a current collector. A Zirfon® separator is used between the two electrolyte compartments. Close to the GDE surface in the catholyte chamber an Ag/AgCl reference electrode is placed.

[0084] The electrolyte solution in all examples below is composed of 0.5 M NaCl. HCl was added until a pH of 3.5 was obtained. Aqueous solutions were prepared of MnCl₂ and CoCl₂ (Sigma Aldrich) with a total metal concentrations ranging from 1 mM to 5.5 mM. Each concentration was prepared for the pure metals, and for mixtures of Mn and Co with varying ratios, and such total metal concentrations. The mixtures prepared contained Mn/Co mole fractions from 0 to 1.

[0085] Anolyte solutions were made in the same way except that no Mn or Co was added, only background electrolyte and HCl for pH control.

[0086] Air was fed into the cell at a flow rate of 1 l h⁻¹ and an overpressure of 18 mbar set by a water column at the gas outlet of the cell. The electrolyte solutions used were 1 l for each anolyte and catholyte. The catholyte solution fed from the catholyte reservoir (fig. 8) and was collected in a separate bottle at the outlet (fig. 8: particle suspension), while the anolyte solution was recirculated to/from the same feed bottle (fig. 8: anolyte reservoir). Peristaltic pumps (Watson-Marlow) were used to provide a liquid flow rate of 20 ml min⁻¹. A current of -300 mA was drawn from the system in a chrono-potentiometry (CP) for each synthesis. The cell has a projected surface area of 10 cm² with a flow channel thickness of 0.4 cm for a total of 4 ml of volume in each chamber. Under these conditions the residence time for incoming Mn²⁺/Co²⁺ ions in the cell is approximately 12 seconds.

[0087] Prior to each synthesis, electrolyte with no transition metal is fed through the reactor in order to wet the electrode and the separator. The inlet of the reactor is then switched from the electrolyte solution, to the catholyte reservoir to begin the synthesis. The CP is started and the outlet pH is monitored until it rises to a steady value. In order to obtain pH data from the very beginning of the experiments, 50 ml of electrolyte solution at pH 3.5 are added to the particle

collection bottle. This allows for enough liquid to wet the pH probe and continuous measurements can be obtained. Once this is achieved, the catholyte outlet is switched to a new collection bottle.

[0088] After this start-up process, the electrochemical reaction was started. Once the experiment was finished and the entire catholyte solution had been consumed, the resulting colloidal suspension was centrifuged (Thermo Scientific Sorvall RC 6+) at 11,000 rpm for 15 minutes. The supernatant solution was removed, and the precipitate washed with a NaOH solution with a pH set to that of the reaction mixture solution at the outlet, and mixed with a vortex. The new mixture was centrifuged again. This process was repeated 3 times to ensure that leftover NaCl from the electrolyte was removed from the particles. Finally, the supernatant was removed once again and the powders are dried under a nitrogen atmosphere at room temperature.

Gas Diffusion Electrode electrochemical studies

[0089] The oxygen reduction reaction (ORR) at the GDE was characterized with Cyclic Voltammetry (CV) and Impedance Electrochemical Spectroscopy (EIS). The supporting electrolyte solution (no transition metals) was used for characterization in the same electrochemical cell, with varying NaCl concentrations (0.25 M and 0.5 M) and varying diffusing gasses (air vs O₂). EIS measurements were taken at potentials between -0.3 V and -0.5 V vs Ag/AgCl on the ORR region of the previously taken CV, between 100 kHz and 10 mHz.

Structural characterization.

[0090] The dry samples were analyzed by powder x-ray diffraction (XRD) in a PanAlytical X'Pert Pro diffractometer (Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$). Samples were crushed in a mortar and placed in standard silicon monocrystals sample holders. Measurements were performed with a spinner at 40 mA-40 kV spending 4 s per step with a step size of $0.04^\circ 2\theta$ in the $10\text{-}110^\circ 2\theta$ range. Rietveld refinements were performed in all samples to fit the profiles and extract the lattice parameters from the data using HighScore Plus software. Crystallite sizes were calculated using the Scherrer equation,

$$\tau = K\lambda / (\beta \cos \theta),$$

with crystallite size (τ), shape factor (K), line broadening factor (β), x-ray wavelength (λ) and Bragg angle (θ).

[0091] Micrographs of the dry samples were taken as is with a FEI Nova NanoSEM 450. Images presented were taken with secondary electrons and an accelerating voltage of 5.00 kV. EDS spectrometry was used to confirm chemical compositions.

Electrocatalytic material testing.

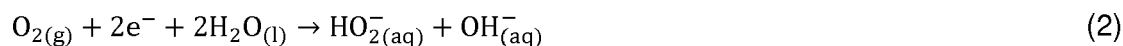
[0092] Inks for electron coating were prepared by dissolving the powders in a mixture of 8 mL of ethanol, 12 mL of DI water and 0.8 mL of a 3% Nafion solution to a final powder concentration of 0.5 mg/mL. The inks were placed in an ultrasonic bath for 30 minutes prior to use. Glassy carbon (GC) disk electrodes were used, 3 mm diameter disks encased in polyether ketone (PEEK) rods with gold contacts. 20 μL of the inks were drop casted on the tip of the rods (6 mm total diameter) and dried in an oven at 40°C for 1 hour. The coated electrodes were dried at room temperature. The electrolyte solution consisted of 250 mL of 1 M KOH. The electrochemical setup consisted of the coated GC as the working electrode, carbon paper as the counter electrode, and Saturated Calomel (SCE) as the reference electrode.

[0093] IR drop is corrected with high frequency impedance prior to measurements. The electrodes are cycled 100 times at 10 mV s⁻¹ between 0.3 V and 0.75 V vs SCE for electrochemical conditioning. After cycling, linear sweep voltammeteries (LSV) were performed at 5 mV s⁻¹ to collect the final data.

Results and Discussion

Electrosynthesis

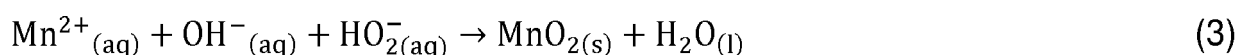
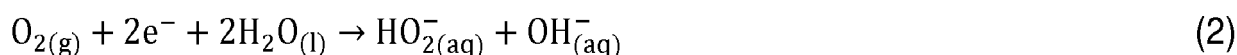
[0094] The electrosynthesis of nanocrystalline mixed Mn-Co oxides/hydroxides proceeds in one step: a feed solution containing MnCl₂ and CoCl₂ metal ion precursor compounds, and 0.5 M NaCl as supporting electrolyte, was fed through a flow cell equipped with a gas diffusion electrode (GDE). Air is flown parallel to the electrode surface, along the hydrophobic side in the gas compartment. Diffusion through the electrode occurs normal to this flow, and reaches a triple phase contact of gas/electrolyte/electrode on the hydrophobic/hydrophilic electrochemically-active interface. The applied potential (-450 mV vs SHE) serves to reduce oxygen and generate reactive oxygen species :



[0095] These reduction products then diffuse out of the porous electrode, towards the electrolyte, reacting at the edge of the diffusion layer with the metal ion precursors in the feed solution. Currents are constant at -30 mA cm⁻² for all experiments. The synthesized materials are collected at the outlet of the catholyte chamber, as particle suspensions. Figure 1a and 9 show a schematic of the setup, highlighting the GDE and the reacting species from the gas phase, to the formation of the crystals in the bulk electrolyte.

[0096] A sample chronoamperometry is shown in figure 2 (bottom). Hydroxide production resulting from the ORR causes the pH evolution. Figure 2 (top) shows the pH profiles with time (charge) for solutions containing 0 mM, 1 mM, 2 mM, 3 mM, 4 mM and 5 mM of MnCl₂. All samples and measurements are taken at steady-state, after the stability region achieved in < 15 minutes.

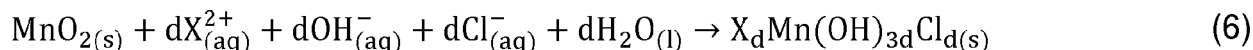
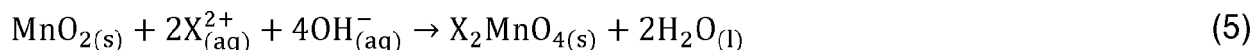
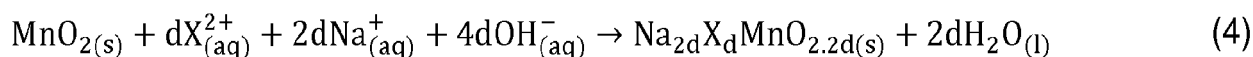
[0097] The current (-30 mA cm⁻²) reduces the incoming molecular oxygen. The first reduction step of the two electron reduction pathway is shown in reactions 1 and 2 for acid and alkaline media respectively. The pH inside the electrode pores rises due to reaction 1, quickly creating an alkaline environment. The peroxide ion can be further reduced at the electrode to hydroxide, or, in the presence of Mn²⁺ can react to oxidize the metal (reaction 3).



[0098] The oxygen reduction reaction fueling the formation of the products was studied on the GD electrode, an uncatalyzed, PTFE-bound, porous carbon electrode. Figure 3 shows the cyclic voltammetry (CV) and impedance results registered at the steady-state polarization conditions (time > 30 min). The oxygen reduction reaction (ORR) was studied from a potential of -0.3 V to -0.5 V vs Ag/AgCl. The impedance spectra show two Gerischer-like semicircles with a high frequency linear segment. The first semi-circle is independent of the applied potential (Fig 3a), oxygen supply (Fig 3b), or electrolyte resistance (Fig 3c). At frequencies between 10 kHz to 100 Hz, this is attributed to the electrode geometry, a behavior characteristic of semi-infinite pores. High frequency signals fail to penetrate the entire depth of the pores, leading to the straight line in the first part of the spectra. The low frequency semi-circle exhibits similar characteristics, but with impedance magnitudes depending on all the previously mentioned parameters. Increasingly negative potentials, higher oxygen supply, and higher electrolyte concentration, all reduce the overall magnitude of impedance. Similar behavior is seen in other triple-phase boundary reactions in gas diffusion electrodes, suggesting a mechanism dependent on the diffusion through deep electrode pores and adsorption of the reactive species (oxygen) before charge transfer occurs and the reaction (1 and 2) products diffuse out of the electrode to start the precipitation process (reaction 3).

Charge driven structural control.

[0099] Control over the synthesized materials may be achieved by varying the amount of charge applied and by varying the precursor solution. A ratio of charge applied to total metal concentration, $R_Q = Q/[M]$, as well as the mole fraction of Co, $X_{\text{Co}} = ([\text{Co}]) / ([\text{Co}] + [\text{Mn}])$, determines unique combinations of structure and composition of the reaction products. Figure 1 shows the structural transitions upon changing RQ and X_{Co}. As the potential, and thus the charge applied, are constant in all the experiments presented, the rate of production of reactive oxygen species (ROS) is the same for all cases. These species (peroxide, superoxide, radicals, etc.) oxidize the metals from 2+ to the target average oxidation state required for each material. R is then controlled by changing the inlet metal precursor concentration, which leads to the target degree oxidation in the products. A higher ratio results in higher average valence of the synthesized materials, with common average oxidation states of the metals: CoMn-LDHs (LDH) +2.3 (reaction 6), Bir-MnO₂ (BIR) +3.7 (reaction 4), and spinels (cubic CSPIN and tetragonal TSPIN) +2.66 (reaction 5). The layered materials result from both extremes of RQ, as the layers can have a majority composition of either Mn(IV)O₂ or Mn(II)(OH)₂, while intermediate oxidation states yield spinels. The proposed formation reactions, starting from the dioxide described by reaction 3, are summarized below:



[0100] A phase diagram (Figure 4a) is composed from experiments carried out with - 30 mA cm⁻². Mn-only containing solutions produce birnessites at concentrations lower than 1.5 mM, and single phase spinels at [Mn] > 2.5 mM. Feed concentrations much larger produce unstable Mn(OH)₂, which quickly oxidizes to the spinel, and results in left over Mn ions in solution, due to insufficient charge for precipitation. Values between the boundaries result in mixed compounds with both phases present. With the addition of cobalt, a new layer of depth is added. Stoichiometry changes reflecting the inlet solution occur until the structural distortions cause too much strain, which leads to the formation of a new phase. Hence the formation of the cubic spinels (CSPIN) and LDHs. At preponderant cobalt fractions, β-hydroxides are formed; not long after production, the structure partially shifts to the α- variety, making the synthesis of single-phase β-Co(OH)₂ difficult.

[0101] Birnessite-type layered Mn dioxide is rarely formed in the absence of small intercalating cations; as such, the large excess of Na⁺ (0.5 M) in the synthesis solution promotes its formation. In addition, the mildly oxidative nature of the synthesis conditions favors the birnessite structure as well, the MnO₂ layers are relatively under-oxidized and electrostatically compensated by the intercalated cations, contrarily to other Mn dioxides (α-, β-, etc.) which include a higher Mn⁴⁺ content. This results in Na-birnessite, Na_xMnO₂. On the opposite end of the spectrum, the excess of Cl⁻ in solution allows the formation of the LDHs over single metal hydroxides when the RQ is low and the metals are mostly un-oxidized. The β-Co(OH)₂ structure is stabilized in the presence of Mn³⁺, forming the Cl- LDH.

[0102] Single- and multi-phase materials were obtained by operating in the specified concentration regions. Diffraction patterns of each region in the phase diagram are presented in figure 4b. Characteristic peaks are marked for each structure, to show the phase purity of BIR, CSPIN, TSPIN and LDH materials, as well the different phase mixtures of the phase transitions. All peaks can be indexed by the respective phase. The tetragonal spinel shown was refined to a I4₁/amd space group. Peak broadening is observed for the cubic spinel (Fd3m), attributed to the (nano-)crystallite size. The BIR and LDH traces are also shown to be phase pure. The shift to small angles in the reflections of the LDH, relative to the BIR, serves as an easy identifier of the hydrotalcite structure. Peak splitting around 65° 2θ, seen as a broad hump in the BIR spectra, points to an orthorhombic structure, as opposed to the naturally-occurring hexagonal birnessite. The peak broadness, present in the LDH pattern to a lesser degree, is a feature of turbostratic structures.

[0103] Micrographs to examine the morphology and dimensions of each structure are shown in Figure 8. Clear distinctions can be made between spinel and layered materials. Spinel exhibit broadly jagged spheres of 15 nm to 35 nm in diameter. Meanwhile, the layered materials can be seen as delaminated sheets, characteristic of turbostratic birnessite, with face dimensions in the range of 50 nm. Brunauer-Emmett-Teller (BET) analysis for the specific surface area of the as-prepared powders resulted in very large values, greater than 70 m² g⁻¹ for all materials synthesized. The large surface area is a feature of the low temperature used to synthesize the materials, as traditional high temperature processes yield larger, more inactive, particles.

Claims

1. An electrochemical process for producing crystalline nanoparticles of a mixed metal oxide, mixed metal hydroxide or mixed metal oxide hydroxide reaction product containing at least a first and a second metal ion which are different from each other, the method comprising the steps of

- (1) supplying to a cathode compartment of an electrochemical cell equipped with a gas diffusion cathode, a liquid feed electrolyte solution containing a first precursor salt of the first metal ion in a first concentration and a second precursor salt of the second metal ion in a second concentration to obtain a reaction mixture;
- (2) supplying an O₂ containing oxidant gas to the cathode,
- (3) subjecting the cathode to an electrochemical potential which is below the thermodynamic limit of O₂ reduction at the pH of the reaction mixture,
- (4) applying a potential to the electrode to cause reduction of the O₂ contained in the oxidant gas to one or more of the corresponding peroxide, OH⁻, ionic and/or radical reactive O containing species,
- (5) wherein a ratio R_Q of charge Q applied to the cathode relative to the sum of the individual concentrations

of the at least one first and second metal ion ($[M_1] + [M_2]$) ranges between 100 and 1500 C/mmol, wherein $[M_1]$ is the concentration of the first metal ion in the reaction mixture and $[M_2]$ is the concentration of the second metal ion in the reaction mixture,

(6) and isolating nanoparticles of the reaction product.

2. A method as claimed in claim 1, wherein the at least one first and second metal ions in the reaction products are either ions of different metal or ions of a same metal having a different oxidation state, or a combination hereof.
3. A process as claimed in claim 1 or 2, wherein a ratio of the concentration of the at least one first and second metal ion to the total metal ion concentration in the feed solution, i.e. $X_{Mi} = [M_i] / \sum [M_n]$, with n being the number of different metal ions in the feed solution, may be varied between 0 and 1.
4. A process as claimed in any one of the previous claims, wherein the electrolyte is supplied to the cathode chamber with a flow rate of between 1 and 250 - 150 ml/min, preferably between 5 and 100 ml/min, more preferably between 5 and 50 ml/min.
5. A method as claimed in any one of the previous claims, wherein the catholyte contains water, an organic solvent, a mixture of two or more organic solvents, a mixture of water with one or more organic solvents.
6. A process as claimed in any one of the previous claims, wherein the oxidant gas flow rate with which the O_2 containing oxidant gas is supplied to the ranges between 5.0 and 300.0 ml/min, preferably between 5.0 and 250.0 ml/min, more preferably between 5.0 and 150.0 ml/min.
7. A process as claimed in any one of the previous claims, wherein the O_2 mole fraction in the oxidant gas ranges between 0.05 and 1.0, preferably between 0.05 and 0.75, more preferably between 0.10 and 0.30.
8. A process as claimed in any one of the previous claims, wherein in the cathode compartment an over pressure is maintained, preferably an overpressure of at least 5 mbar.
9. A process as claimed in any one of the previous claims, wherein in the course of the reaction an aqueous solution comprising a supporting electrolyte is supplied to the cathode chamber.
10. A process as claimed in any one of the previous claims, wherein the catholyte contains a supporting electrolyte, in a concentration of between 5.0 and 150.0 g/l of catholyte, preferably between 10.0 and 100 g/l, more preferably between 10.0 and 50.0 g/l.
11. A process as claimed in any one of the previous claims, wherein at the start of the reaction the pH of the reaction mixture is adjusted to a value between 2.0 and 6.0.
12. A process as claimed in any one of the previous claims, wherein the current density applied to the gas diffusion electrode ranges between 10 and 1000 Am^{-2} , preferably between 10 and 500 Am^{-2} , more preferably between 25 and 250 Am^{-2} .
13. A process as claimed in any one of the previous claims, wherein the first and second metal ion may independently of each other be selected from the elements of Group I, Group II, Group III, the transition metals and the lanthanides of the Periodic System of the Elements and mixtures of two or more hereof, preferably the transition metals are selected from the group of Li, Al, Co, Mn, Ni, Fe, Zn, Cu, one or more of the Pt group metals, or a mixture containing two or more hereof
14. A mixed metal oxide or hydroxide obtained with the process of any one of claims 1-13, having a crystal structure selected from the group of birnessite, a layered double hydroxide, a layered double oxide, a layered product, a cubic spinel, a tetragonal spinel, a garnet.

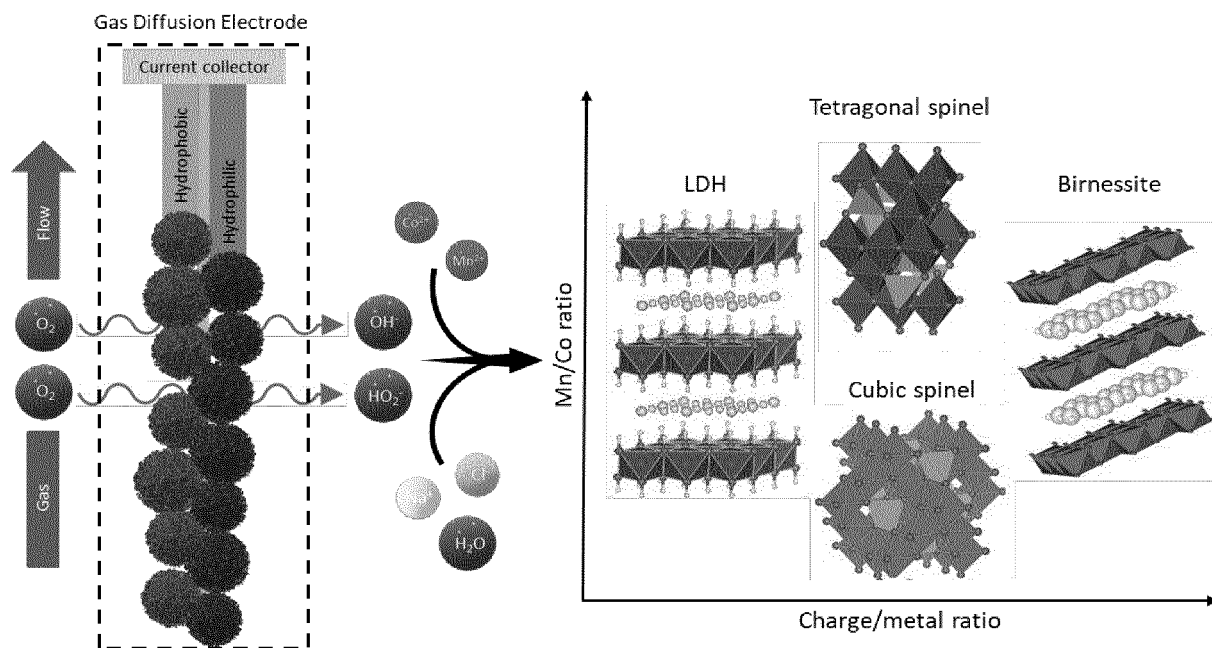


Figure 1a

Figure 1b

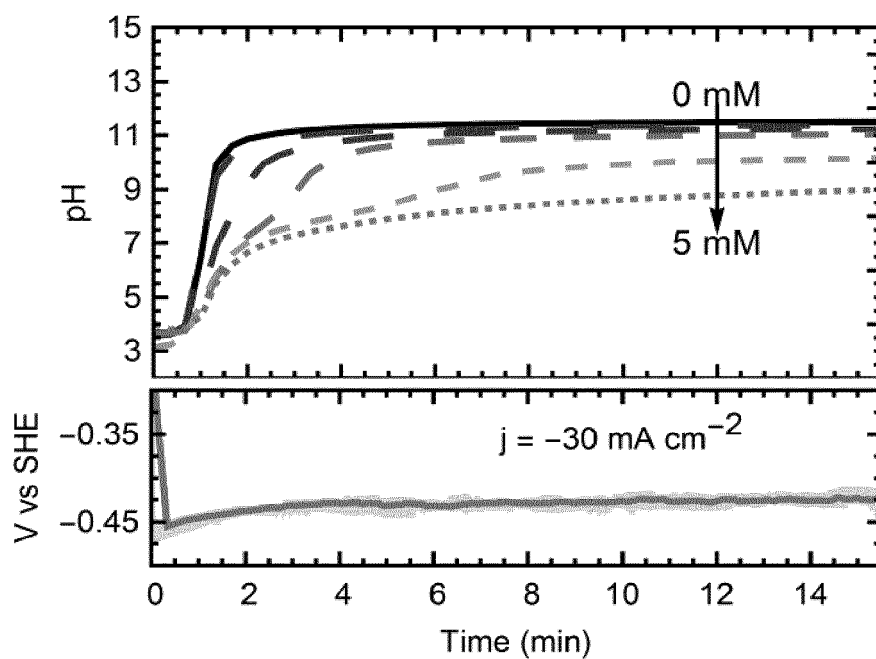


Figure 2a

Figure 2b

Figure 2

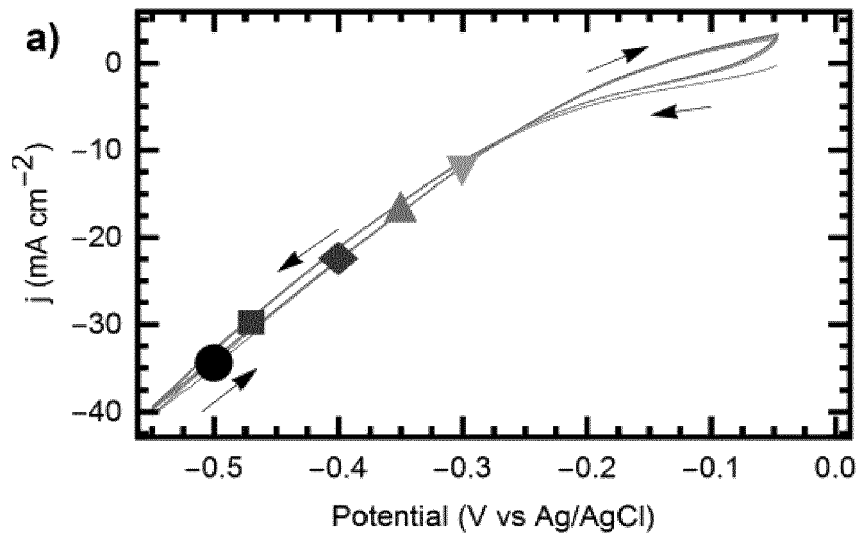


Figure 3a

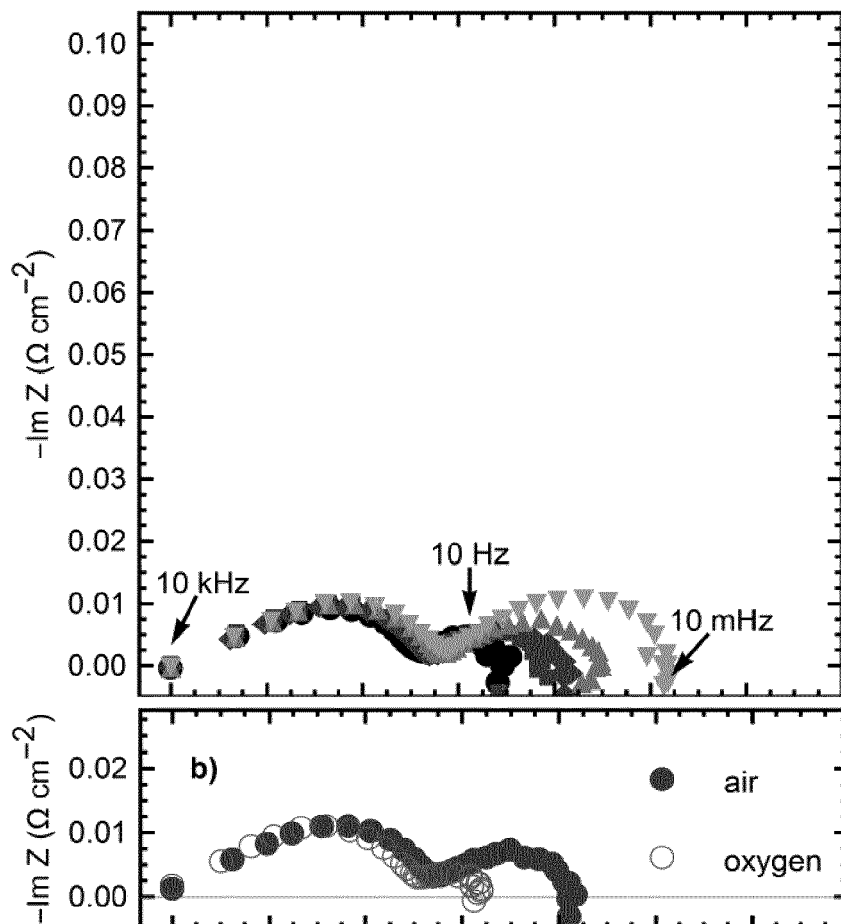


Figure 3b

Figure 3c

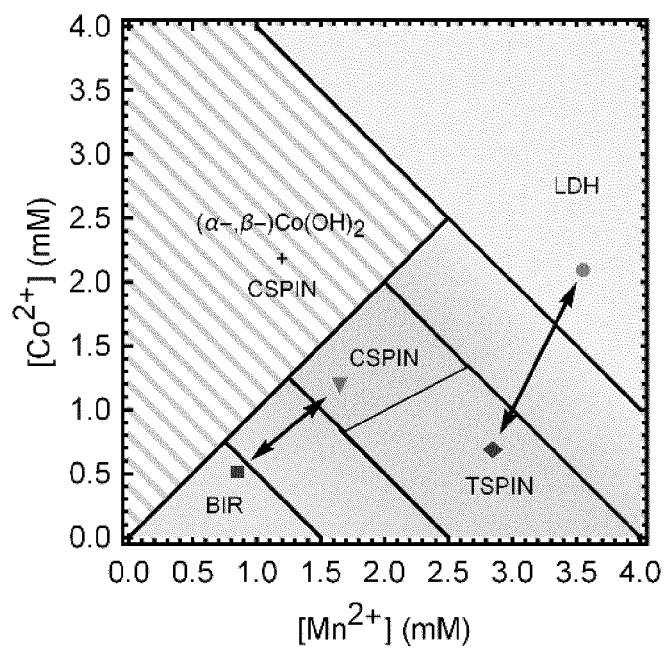


Figure 4a

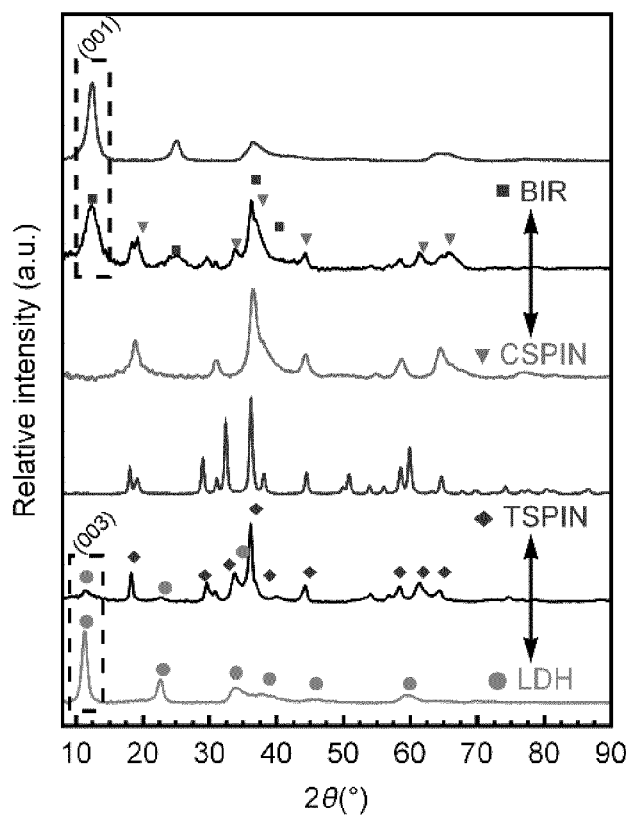


Figure 4b

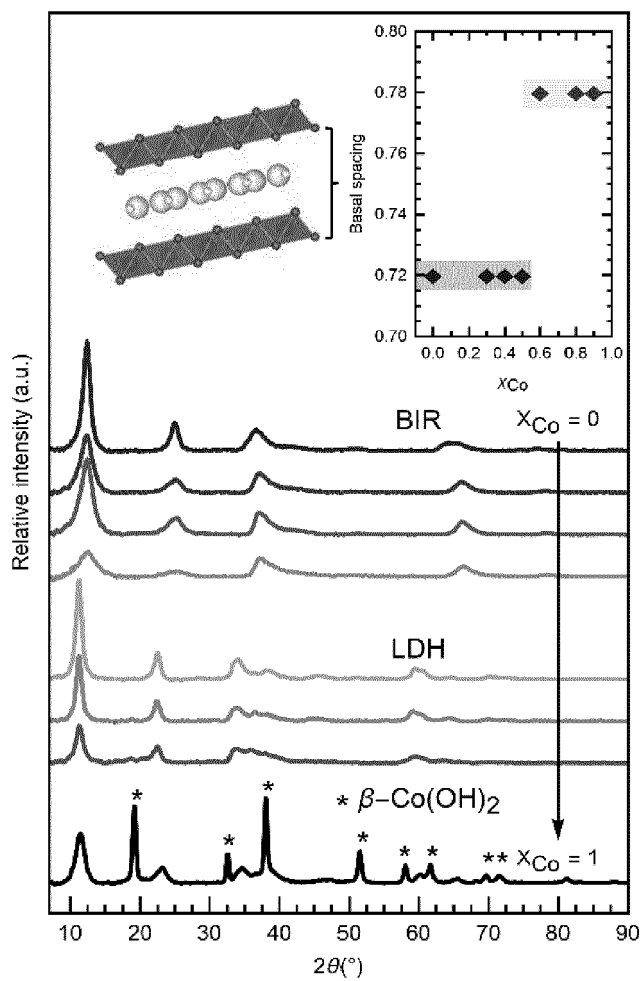


Fig. 5.

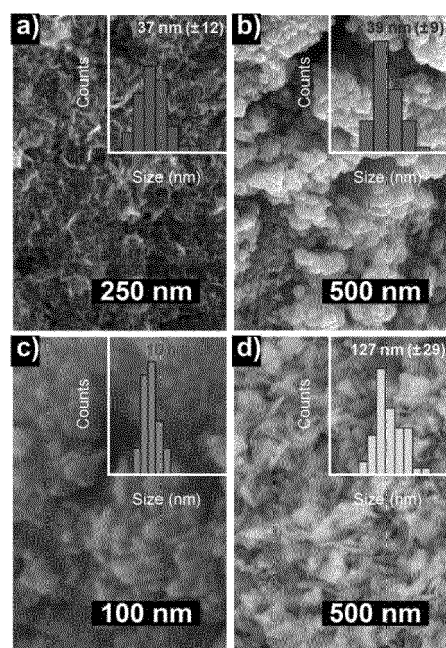


Fig. 8.

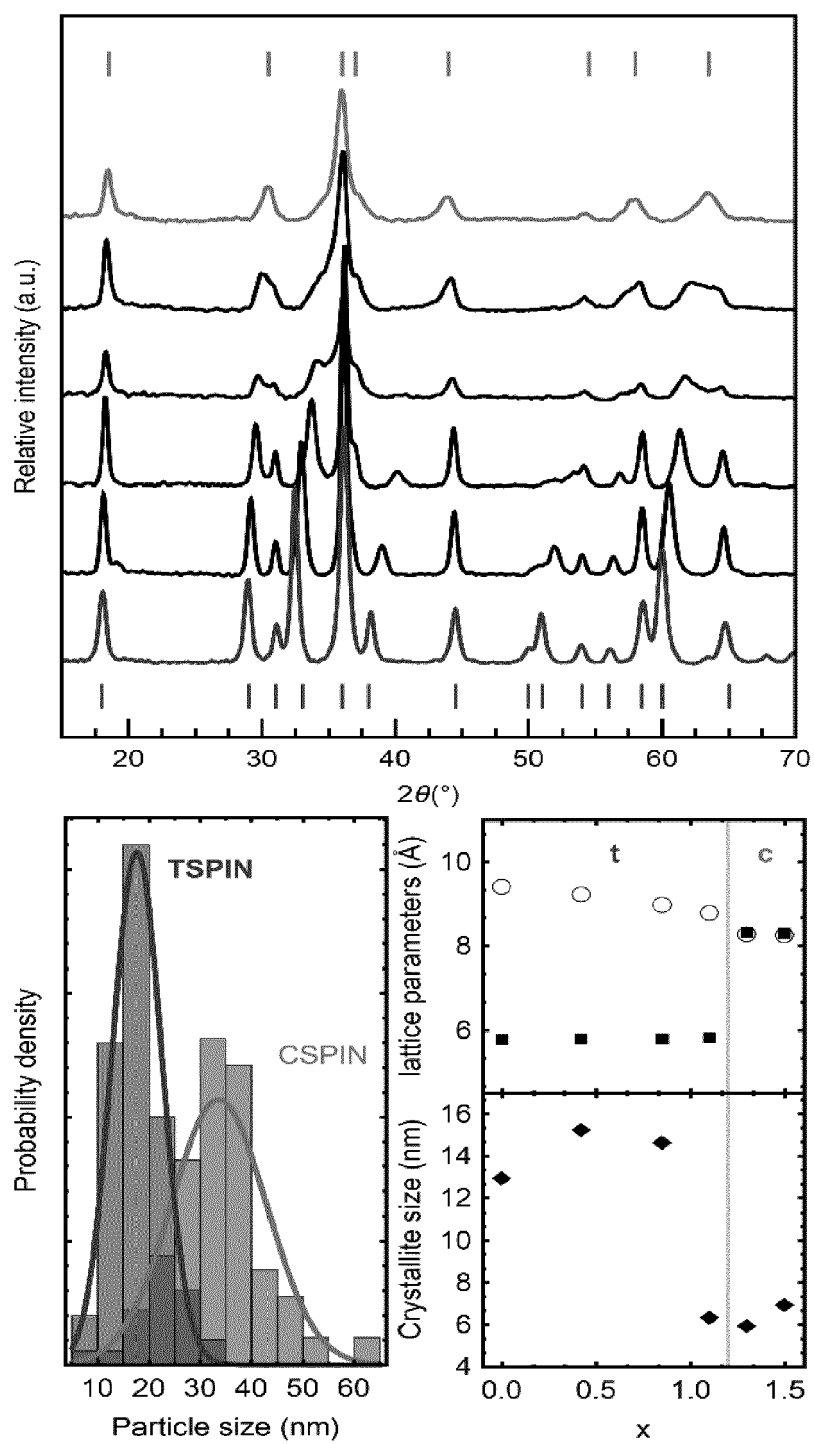


Fig. 6

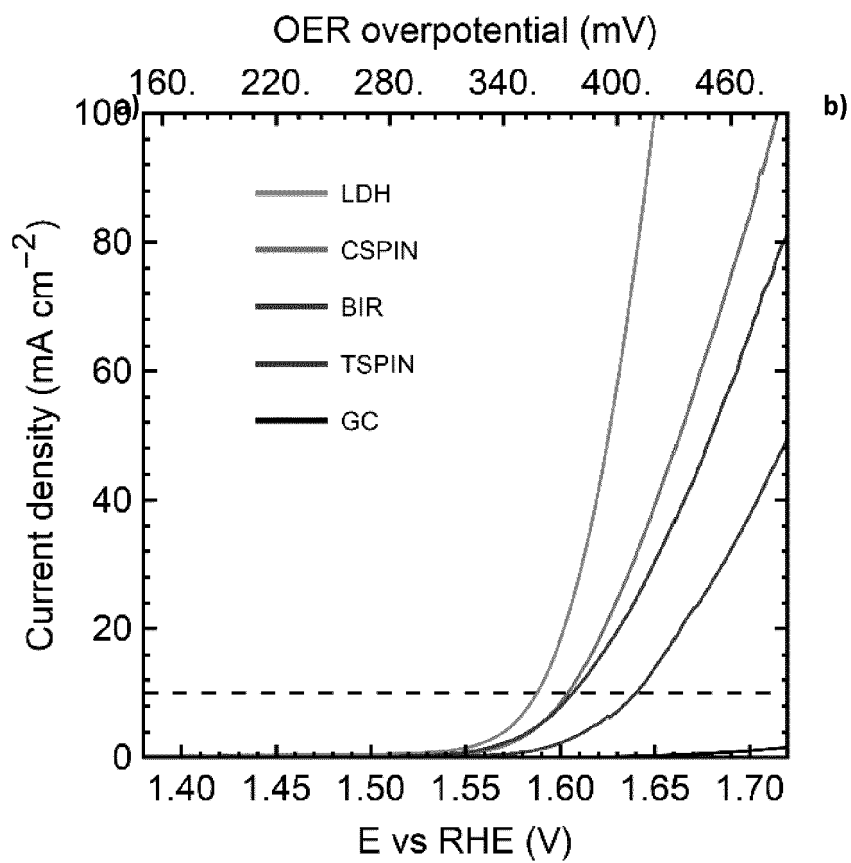


Fig. 7a

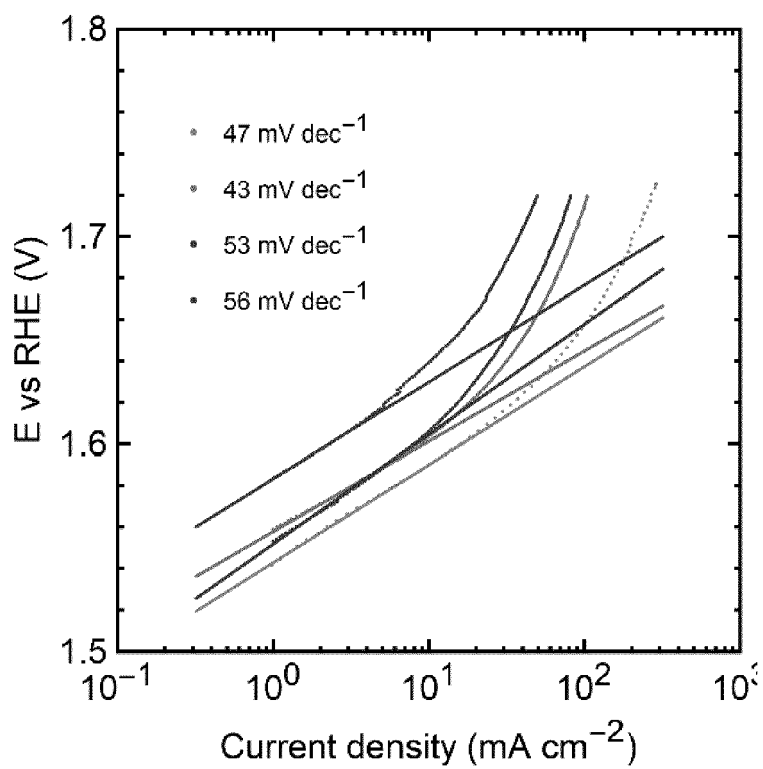


Fig. 7b

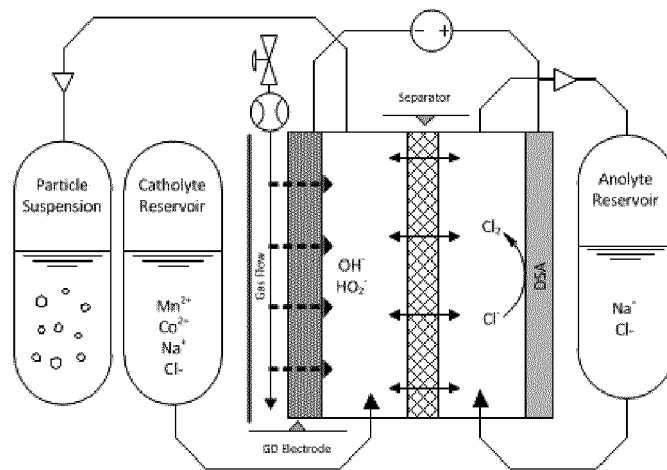


Fig. 9



EUROPEAN SEARCH REPORT

Application Number
EP 19 02 0520

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	EP 3 242 963 A1 (VITO NV [BE]) 15 November 2017 (2017-11-15) * the whole document *	1-13	INV. C25B1/21
A	US 3 073 763 A (BERNARD BEER HENRI) 15 January 1963 (1963-01-15) * the whole document *	1-13	
X	WO 2018/223054 A1 (UNIV CONNECTICUT [US]) 6 December 2018 (2018-12-06) * abstract; claims 1-17 *	14	
X,D	LAVELA ET AL: "Sol-gel preparation of cobalt manganese mixed oxides for their use as electrode materials in lithium cells", ELECTROCHIMICA ACTA, ELSEVIER, AMSTERDAM, NL, vol. 52, no. 28, 25 August 2007 (2007-08-25), pages 7986-7995, XP022214055, ISSN: 0013-4686, DOI: 10.1016/J.ELECTACTA.2007.06.066 * 2. Experimental and 3. Results and discussion *	14	TECHNICAL FIELDS SEARCHED (IPC) C25B
X,D	YONGYE LIANG ET AL: "Covalent Hybrid of Spinel Manganese-Cobalt Oxide and Graphene as Advanced Oxygen Reduction Electrocatalysts", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 134, no. 7, 23 January 2012 (2012-01-23), pages 3517-3523, XP055461587, US ISSN: 0002-7863, DOI: 10.1021/ja210924t * abstract * * Results and Discussion *	14	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 12 March 2020	Examiner Leu, Oana
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P04C01)



EUROPEAN SEARCH REPORT

Application Number
EP 19 02 0520

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	XIE LIJING ET AL: "CoxNi1-xdouble hydroxide nanoparticles with ultrahigh specific capacitances as supercapacitor electrode materials", ELECTROCHIMICA ACTA, vol. 78, 18 June 2012 (2012-06-18), pages 205-211, XP028931893, ISSN: 0013-4686, DOI: 10.1016/J.ELECTACTA.2012.05.145 * abstract * * 2. Experimental *	14	
X,D	WO 2012/150460 A1 (ISIS INNOVATION [GB]; O'HARE DERMOT [GB]; WANG CHENGLE [GB]) 8 November 2012 (2012-11-08) * abstract; claims 1-14 *	14	
X,D	CN 102 976 373 A (UNIV BEIJING CHEMICAL) 20 March 2013 (2013-03-20) * the whole document *	14	
			TECHNICAL FIELDS SEARCHED (IPC)
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 12 March 2020	Examiner Leu, Oana
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 19 02 0520

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-03-2020

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 3242963 A1	15-11-2017	CA 2973289 A1	14-07-2016
		CN 107532309 A	02-01-2018
		DK 3242963 T3	14-01-2019
		EP 3042981 A1	13-07-2016
		EP 3242963 A1	15-11-2017
		ES 2702082 T3	27-02-2019
		JP 2018508659 A	29-03-2018
		US 2018023201 A1	25-01-2018
		WO 2016110597 A1	14-07-2016

US 3073763 A	15-01-1963	NONE	

WO 2018223054 A1	06-12-2018	US 2020061591 A1	27-02-2020
		WO 2018223054 A1	06-12-2018

WO 2012150460 A1	08-11-2012	NONE	

CN 102976373 A	20-03-2013	NONE	

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- CN 102976373 A [0009]
- CN 102976373 [0009]
- KR 101415729 B1 [0010]
- WO 2012150460 A [0011]
- EP 3242963 B1 [0012]

Non-patent literature cited in the description

- **WU ; BAI ; FENG ; XIONG.** Porous mixed metal oxides: design, formation mechanism, and application in lithium-ion batteries. *Nanoscale*, 2015, vol. 7 (41), 17211-17230 [0002]
- **JOHNSON, E. A. ; POST, J. E.** Water in the interlayer region of birnessite: Importance in cation exchange and structural stability. *American Mineralogist*, 2006, vol. 91, 609-618 [0003]
- **NAM, K. W. et al.** The high performance of crystal water containing manganese birnessite cathodes for magnesium batteries. *Nano letters*, 2015, vol. 15, 4071-4079 [0003]
- **XIE, L. et al.** Co x Ni 1- x double hydroxide nanoparticles with ultrahigh specific capacitances as supercapacitor electrode materials. *Electrochimica Acta*, 2012, vol. 78, 205-211 [0004]
- **CHENG, F. et al.** Rapid room-temperature synthesis of nanocrystalline spinels as oxygen reduction and evolution electrocatalysts. *Nature chemistry*, 2011, vol. 3, 79 [0006]
- **ZHOU, L. ; ZHAO, D. ; LOU, X. W.** Double-shelled CoMn₂O₄ hollow microcubes as high-capacity anodes for lithium-ion batteries. *Advanced Materials*, 2012, vol. 24, 745-748 [0006]
- **LIANG, Y. et al.** Covalent hybrid of spinel manganese-cobalt oxide and graphene as advanced oxygen reduction electrocatalysts. *Journal of the American Chemical Society*, 2012, vol. 134, 3517-3523 [0006]
- **LAVELA, P. ; TIRADO, J. ; VIDAL-ABARCA, C.** Sol-gel preparation of cobalt manganese mixed oxides for their use as electrode materials in lithium cells. *Electrochimica Acta*, 2007, vol. 52, 7986-7995 [0006]
- **LI, C. et al.** Phase and composition controllable synthesis of cobalt manganese spinel nanoparticles towards efficient oxygen electrocatalysis. *Nature communications*, 2015, vol. 6, 7345 [0006]
- **KAI, K. et al.** Room-temperature synthesis of manganese oxide monosheets. *Journal of the American Chemical Society*, 2008, vol. 130, 15938-15943 [0006]
- **SONG, F. ; HU, X.** Ultrathin cobalt-manganese layered double hydroxide is an efficient oxygen evolution catalyst. *Journal of the American Chemical Society*, 2014, vol. 136, 16481-16484 [0006]
- **KATSOUNAROS, I. ; CHEREVKO, S. ; ZERADJANIN, A. R. ; MAYRHOFER, K. J.** Oxygen electrochemistry as a cornerstone for sustainable energy conversion. *Angewandte Chemie International Edition*, 2014, vol. 53, 102-121 [0006]
- **CHENG, F. ; CHEN, J.** Metal-air batteries: from oxygen reduction electrochemistry to cathode catalysts. *Chemical Society Reviews*, 2012, vol. 41, 2172-2192 [0007]