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(54) **Title:** A METHOD OF SYNTHESIS OF TRANSITION METAL NITRIDES AND THEIR USE WHEN THEY HAVE TWO, THREE OR FOUR METALS AS CATALYSTS FOR THE OXYGEN EVOLUTION REACTION

(57) **Abstract:** The present invention discloses a new up-scalable synthesis of heterogeneous transition metal nitrides (TMNs) using the carbonate salts as precursors. The synthesis leads to highly heterogeneous materials that are obtained in quantitative yields without the use of solvents or reagents other than anhydrous NH_3. In addition, the TMNs with between at least two and up to four metals shows catalytic behaviour in the oxygen evolution reaction (OER).

A METHOD OF SYNTHESIS OF TRANSITION METAL NITRIDES AND THEIR USE WHEN THEY HAVE TWO, THREE OR FOUR METALS AS CATALYSTS FOR THE OXYGEN EVOLUTION REACTION.

The present invention discloses a new up-scalable synthesis of heterogeneous transition metal nitrides (TMNs) using the carbonate salts as precursors. The synthesis leads to highly heterogeneous materials that are obtained in quantitative yields without the use of solvents or reagents other than anhydrous NH_3. In addition, the TMNs with between at least two and up to four metals shows catalytic behaviour in the oxygen evolution reaction (OER).

BACKGROUND ART

Transition metal nitrides (TMNs) are considered to be promising electrode materials for many devices, such as supercapacitors, due to their physical, chemical, and mechanical properties, low cost, excellent electronic conductivity, high stability at higher temperatures, and good chemical resistance. They exhibit high catalytic activity, distinctive electronic structures, and enhanced surface morphologies. Specifically, several ternary TMNs have been reported as highly efficient, stable and cost-effective electrocatalysts for oxygen evolution reaction (OER), which is critical for a range of renewable-energy technologies, including metal-air batteries, fuel cells and water-splitting reactions.

In general, TMNs can be prepared by maintaining a nitrogen rich atmosphere over metal-based precursors. TMNs can be prepared from metal materials by direct calcination in the N_2 atmosphere at high temperatures above 1200 ºC. As an example, vanadium nitride can be prepared at 1200 °C from metal powder or film by passing N_2 gas. The disadvantage of this direct synthetic route is the limitation to a few stable nitrides because the process is limited by large thermodynamic barriers which are due to the making and breaking of the triple bond in dinitrogen (945 kJ mol^{-1}). Therefore, it is reported that this method is suitable only for highly thermally stable nitrides. Therefore, most nitrides are prepared by ammonothermal method at present. This method uses metal powder, oxides, hydroxide, halides, and sulfides, etc. as metal-based precursors in an ammonia atmosphere at certain temperatures enable the synthesis of corresponding TMNs.

In addition to nitrogen or ammonia, nitrogen-based compounds like urea have been used as nitrogen sources for the synthesis of TMNs. When urea is used as the nitrogen source, ethanol is usually used to dissolve metal salts. But in some cases, metal salts do not

dissolve in ethanol. If urea is added to it, dissolution increases. [Cheng et al, Adv. Funct. Mater. 2021, 2100553]

Thus, a problem to be solved is finding a synthetic method that allows the production of single and multi-transition metal nitrides in a single step without the use of solvents and allowing the upscaling of the production and at temperatures equal or lower than 1200 ºC.

SUMMARY OF THE INVENTION

The process of the present invention described herein is a method for synthesizing multimetallic transition metal nitrides (TMNs) in a single step using the metal salt precursors. Transition metal salts based on Ni, Co, Fe, Ga, Al, Ti, Zn and Mn can be mixed in specific desired stoichiometric ratios. These precursor powders can then be converted from the salt to the nitride in a tube furnace reactor with flowing of anhydrous ammonia at temperatures ranging from 350 to 1200 °C and times ranging from 1 to 24 hours.

The advantages of the direct nitridation of the carbonate salts disclosed herein, is the ease of synthesis in a single, high-yield (quantitative) step. Additionally, given that the carbonate salts of these metals are an inexpensive source of the transition metal, the cost of scaling this reaction to industrial levels is minimal compared to the synthesis procedure used for other, mixed metal oxide catalysts. For example, the synthesis of the mixed metal oxides requires the use of the metal acetate salts, have yields in the 10-30% range (based on metals), and have aqueous waste containing unreacted metal precursors which must be processed for proper disposal. On the other hand, the nitridation reaction described herein gives no liquid waste for disposal because the reaction is done using gaseous NH_3 with solid salts and solid TMN product.

The present invention discloses a novel method for the synthesis of transition metal nitrides characterized in that comprising the following steps:

a) providing at least one precursor transition metal salts $M_x(A)_z$, wherein:
M is a transition metal;
A is CO_3^{2-} or $CH_3CO_2^-$;
wherein x is 1 or 2; and wherein z is the valence or mixed valences of the transition metal of the chosen precursor;

with a ratio according to the expected stoichiometry of the metal or metals in the transition metal nitride;

b) grinding the transition metal salts; and

c) heating with a ramp temperature of between 8.75 ºC/min and 20ºC/min for a time of between 40 min and 70 min up to reach an annealing temperature of between 350 and 1200 °C the grinded transition metal salt of step (b) with NH_3 for nitridation at the annealing temperature for a period between 1 and 24 hours, and preferably for a period between 2 and 10 hours.

In another embodiment the method does not comprise the adding of tannin and/or the method does not comprise any further heating at a temperature over 40 ºC.

In another embodiment the method consists of the step (a) to (c) previously mentioned.

In the present invention the term "tannin" as used herein refers to a substance that is easily dissolved in water, whose aqueous solution is highly astringent, and which has the property of tanning leather, and is conventionally known by the generic name of tannin. Chemically, tannin is not a simple substance but an aggregation of complex organic polyphenolic compounds. Generally, tannins are extracted with warm water or hot water as an extraction agent is used as a base agent, and if required, tannin may be further purified with an organic solvent or modified with alkalis or the like. There are two main classes of tannins: hydrolyzable tannins and condensed tannins.

Condensed tannins are found in virtually all families of plants and constitute more than 90% of the total world production of commercial tannins. They are known for their wide distribution in nature, in particular in wood and bark of various trees, and comprise up to 50% of the dry weight of leaves. Condensed tannins are polymerized to generate phlobaphene that is insoluble in water and reacts with aldehyde to become a polymer. Due to this property, condensed tannins, in particular tannin formaldehyde resins have been used as an adhesive or a binder for wood from the latter half of 1960s.

Hydrolyzable tannins, on the other hand, are derivatives that are hydrolyzed by heating with a dilute acid to generate gallic acid (3,4 5-trihydroxyl benzoic acid). In the present invention a tannin is for example, without limit, gallic acid, tannic acid and Gallotannin.

In one embodiment, the heating of step (c) takes place under a flow of NH_3 for nitridation with a flow rate between 50 and 1000 mL/min, and preferably between 50 and 100 mL/min,

more preferably 100 mL/min. Lower flow is better because less ammonia would be used and up to 100 ml/L the management is without safety concerns.

In a further embodiment, the transition metal M is selected from Ni, Co, Fe, Ga, Al, Ti, Zn, Mn and any combination thereof, preferably from Fe, Ni, Co, Mn and any combination thereof.

In a further embodiment in the step (a) at least two precursors transition metal salts are provided.

In a further embodiment, the step (b) further comprising a mixing of the transition metal salts before the grinding.

The use of a two or more transition metal salt precursor with a ratio according to the expected stoichiometry of the metals in the transition metal nitride give a multi transition metal nitride.

In a preferred embodiment of the method two different precursor transition metal salts Mx(A)z of step (a) are used with a ratio according to the expected stoichiometry of the metals in the transition metal nitride to form binary transition metal nitrides.

In another preferred embodiment three or four different precursor transition metal salts Mx(A)z of step (a) are used with a ratio according to the expected stoichiometry of the metals in the transition metal nitride to form ternary or quaternary transition metal nitrides.

In another preferred embodiment up to 7 different precursor transition metal salts Mx(A)z are used with a ratio according to the expected stoichiometry of the metals in the transition metal nitride to form a transition metal nitrides with a combination of the seven metals and nitride phases.

In another preferred embodiment the grinding of step (b) is by ball milling at a velocity of between 10 Hz and 30 Hz, preferably 20 Hz, for a time between 10 min and 50 min, preferably between 15 and 25 min.

A second aspect of the present invention is the transition metal nitrides obtained by the

method described above wherein the transition metal nitride that has an amorphous phase of at least a 2% in weight in respect of the total composition. Preferably the transition metal nitrides are selected from the list of table 1.

In a preferred embodiment the multi transition metal nitrides comprising two or more transition metals. In a more preferred embodiment the transition metals are selected from the list Ni, Co, Fe. In an even more preferred embodiment, the nitride is $Co_{90}Fe_{10}N_x$, $Co_{90}Ni_{10}N_x$, $Ni_{90}Fe_{10}N$ or $Ni_{90}Co_{10}N_x$.

The term "N_x or x as a subindex of nitrogen stoichiometry" as used herein refers to the amount of nitrogen in the mixed metal nitrides is variable, and not even quantifiable. Indeed, some of the nitrides have small, substoichiometric amounts of nitrogen that is doped into the otherwise metallic lattice.

In a preferred embodiment the multi transition metal nitrides comprising three or more transition metals. In a more preferred embodiment, the transition metals are selected from Ni, Co, Fe, Mn and Zn. In an even more preferred embodiment, the nitride is $Co_{45}Ni_{45}Fe_{10}N_x$, $Ni_{60}Co_{30}Fe_{10}N$, $Ni_{33}Co_{33}Fe_{33}N$, $Ni_{90}Co_5Fe_5N_x$, $Co_{90}Fe_5Ni_5N_x$, $Co_{57}Ni_{14}Fe_{29}N_x$, $Ni_{99}Co_{0.3}Fe_{0.3}Mn_{0.3}N_x$, or $Co_{90}Ni_{3.3}Fe_{3.3}Mn_{3.3}N_x$.

In an even more preferred embodiment, the multi transition metal nitride (multi TMN) is $Co_{45}Ni_{45}Fe_{10}N_x$. The compound shows more than double the current density

The third aspect of the present invention is the use of the transition metal nitrides with two, three or four metals described above as a catalyst for the oxygen evolution reaction

The characterization of the materials was done by powder XRD (PXRD). Precise determination of the phases detected in the PXRD patterns for multi metal transition metal nitrides are difficult for several reasons: first, the peaks of the different phases are very close, second the peaks are often weak and very broad, making distinction of these phases difficult.

The majority of the samples had at least 2% of amorphous material in weight in respect of the total composition and often included more than one nitride phase indicating the

heterogeneity of this synthesis method and the unique materials exhibiting advantageous properties for OER catalysts due to this heterogeneity.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skilled in the art to which this invention belongs. Methods and materials similar or equivalent to those described herein can be used in the practice of the present invention. Throughout the description and claims the word "comprise" and its variations are not intended to exclude other technical features, additives, components, or steps. Additional objects, advantages and features of the invention will become apparent to those skilled in the art upon examination of the description or may be learned by practice of the invention. The following examples, drawings and sequence listing are provided by way of illustration and are not intended to be limiting of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1. Powder X Ray Diffraction (PXRD) of Ni_3N

Fig. 2. PXRD of Fe_3N

Fig. 3. PXRD of GaN

Fig. 4. PXRD of AlN

Fig. 5. PXRD of TiN_x

Fig. 6. PXRD of $Co_{90}Fe_{10}N_x$

Fig. 7. PXRD of $Ni_{90}Fe_{10}N$

Fig. 8. PXRD of $Co_{45}Ni_{45}Fe_{10}N_x$

Fig. 9. HRTEM/EELS of $Co_{45}Ni_{45}Fe_{10}N_x$

Fig. 10. PXRD of $Co_{57}Ni_{14}Fe_{29}N_x$

Fig. 11. PXRD of $Co_{9,0}Ni_{3.3}Fe_{3.3}Mn_{3.3}N$

Fig. 12. Cyclic voltammogram of CoN_x, NiN_x, FeN_x, $Co_{45}Ni_{45}Fe_{10}N_x$, $Co_{57}Ni_{14}Fe_{29}N_x$, in comparison with state-of-the-art catalysts $NiCoFeO_x$ and commercially available IrO_x

Fig. 13. Polarization curve conducted at 1 mV/s conducted in 0.1 M KOH, and unless otherwise stated, 65 °C of $Co_{45}Ni_{45}Fe_{10}N_x$ in comparison with state-of-the-art catalysts $NiCoFeO_x$ and commercially available IrO_x

Fig. 14. Chronoamperometry at 1.8 V of $Co_{45}Ni_{45}Fe_{10}N_x$ in comparison with state-of-the-art catalysts $NiCoFeO_x$ and commercially available IrO_x

EXAMPLES

Example 1: General synthetic route

For the synthesis of TMNs from the volatile salt precursors, the pure precursors M(A) (where M= Ni, Co, Fe, Ga, Al, Ti, Zn, Mn, and A= CO_3^{2-} or $CH_3CO_2^-$), or a chosen stoichiometric mixture (0.5-2 gram total) was ground in a mortar and pestle, or ball milled, before being placed in a ceramic sample holder. In order to know the used masses it is based on the percent by mass of metal in the carbonate salt precursor determined by digesting the carbonate salts in sulfuric acid and conducing ICP. The precursor powder was then placed into the quartz tube reactor flushed with N_2, then NH_3 was flowed at a rate of 100 mL/min using a mass flow controller. The quartz tube was heated from room temperature to the final temperature (between 375 and 1200 °C) over one hour then maintained for 6 hours. The reactor was allowed to cool in an NH_3 atmosphere before being flushed with N_2 prior to removal of the sample.

While the crystallinity varied, the yields of the samples were always quantitative with respect to the metal. In the table below is a summary of the mixed metal nitrides synthesized, characterized by PXRD results.

Table 1: Indicative list of transition metal nitrides successfully prepared by the disclosed method.

Fe_3N	1 metal

MnN_x	
CoN_x	
Ni_3N	
CrN	
AlN	
GaN	
TiN_x	
ZnN_x	
$Co_{90}Fe_{10}N_x$	2 metals
$Co_{90}Ni_{10}N_x$	
$Ni_{90}Fe_{10}N_x$	
$Ni_{90}Co_{10}N_x$	
$Ni_{33}Co_{33}Fe_{33}N_x$	3 metals
$Ni_{90}Co_5Fe_5N_x$	
$Ni_{60}Co_{30}Fe_{10}N_x$	
$Ni_{45}Co_{45}Fe_{10}N_x$	
$Co_{45}Ni_{45}Fe_{10}N_x$	
$Co_{57}Ni_{14}Fe_{29}N_x$	
$Co_{90}Fe_5Ni_5N_x$	
$Ni_{99}Co_{0.3}Fe_{0.3}Mn_{0.3}N_x$	4 metals
$Co_{90}Ni_{3.3}Fe_{3.3}Mn_{3.3}N_x$	

On the following examples, the synthesis procedure is shown for Ni_3N, Fe_3N, GaN, AlN, TiN, MnN_x, CrN, CoN_x, ZnN_x, $Co_{90}Fe_{10}N_x$, $Ni_{90}Fe_{10}N_x$, $Ni_{90}Co_{10}N_x$, $Co_{45}Ni_{45}Fe_{10}N_x$, $Ni_{60}Co_{30}Fe_{10}N_x$, $Ni_{33}Co_{33}Fe_{33}N_x$, $Ni_{90}Co_5Fe_5N_x$, $Co_{90}Fe_5Ni_5N_x$, $Co_{90}Ni_{3.3}Fe_{3.3}Mn_{3.3}N_x$. In the cases of Ni_3N, Fe_3N, CrN, GaN, AlN, has been obtained a known phase-pure nitride. Note that when it is said phase pure, that does not mean that we observed zero amorphous, it has an amorphous of at least 2%, but it means that we had no mixed phases and did not observe any precursor or any other oxide or nitride phases.

Ni_3N

To obtain this material, 0.5 gram of $Ni(OAc)_2$ grinded was placed in a ceramic holder . With a NH_3 flow rate of 100 mL/min the sample was heated to 420 °C over 1 h and the temperature was maintained for 2 h. The material was characterized by PXRD in Fig.1

Fe_3N

To obtain this material, 1 gram of $Fe(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 600 °C and maintained the temperature for 6 hours. The material was characterized by PXRD in Fig.2

GaN

To obtain this material, 1 gram of $Ga(OAc)_3$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 900 °C and maintained the temperature for 2 hours. The material was characterized by PXRD in Fig.3

AlN

To obtain this material, 1 gram of $Al(OAc)_3$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 1000 mL/min the sample was heated to 1200 °C and maintained the temperature for 10 hours. Note that earlier attempts at lower time/temp led material that contained some AlN but the crystallinity was low and the peaks were broad. The material was characterized by PXRD as in Fig.4

TiN_x

To obtain this material, 1 gram of $Ti(OAc)_4$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 800 °C and maintained the temperature for 6 hours. The resulting material has peaks consistent with TiN but also contains a large portion of peaks that are consistent with TiO_2. The material was characterized by PXRD as in Fig.5

MnN_x

To obtain this material, 0.5 gram of $Mn(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 400 °C with a ramp temperature of 6.7 ºC/min and maintained the temperature for 2 hours.

CoN_x

To obtain this material, 1 gram of $Co(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 900 °C with a ramp temperature of 6.7 ºC/min and maintained temperature for 6 hours.

CrN

To obtain this material, 1 gram of $Cr(OAc)_2$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 500 mL/min the sample was heated to 425 °C with a ramp temperature of 6.7 ºC/min and maintained temperature for 6 hours.

ZnN_x

To obtain this material, 1 gram of $Zn(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 425 °C with a ramp temperature of 6.7 ºC/min and maintained temperature for 6 hours.

$Co_{90}Fe_{10}N_x$

To obtain this material, 0.146 gram of $Fe(CO_3)\cdot nH_2O$ and 0.854 gram of $Co(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 450 °C with a ramp temperature of 8.5 ºc/min for 50 min and maintained at that temperature for 6 hours. The material was characterized by PXRD as in Fig. 6. Its advantageous properties for OER catalysts when compared with homometallic nitrides as shown in Fig. 6.

$Ni_{90}Fe_{10}N$

To obtain this material, 0.122 gram of $Fe(CO_3)\cdot nH_2O$ and 0.878 gram of $Ni(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 420 °C with a ramp temperature of 8 ºc/min for 50 min and maintained at that temperature for 2 hours. The material was characterized by PXRD as in Fig. 7.

$Co_{90}Ni_{10}N_x$

To obtain this material, 0.146 gram of $Ni(CO_3)\cdot nH_2O$ and 0.854 gram of $Co(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 420 °C with a ramp temperature of 8 ºc/min for 50 min and maintained at that temperature for 2 hours.

$Ni_{90}Co_{10}N_x$

To obtain this material, 0.878 gram of $Ni(CO_3)\cdot nH_2O$ and 0.122 gram of $Co(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 420 °C with a ramp temperature of 8 ºc/min for 50 min and maintained at that temperature for 2 hours.

$Ni_{60}Co_{30}Fe_{10}N$

To obtain this material, 0.620 gram of $Ni(CO_3)\cdot nH_2O$, 0.252 gram of $Co(CO_3)\cdot nH_2O$ and 0.129 gram of $Fe(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 425 °C with a ramp temperature of 6.7 ºc/min for 60 min and maintained at that temperature for 6 hours.

$Ni_{33}Co_{33}Fe_{33}N$

To obtain this material, 0.327 gram of $Ni(CO_3)\cdot nH_2O$, 0.266 gram of $Co(CO_3)\cdot nH_2O$ and 0.407 gram of $Fe(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 425 °C with a ramp temperature of 6.7 ºc/min for 60 min and maintained at that temperature for 6 hours.

$Ni_{90}Co_5Fe_5N_x$

To obtain this material, 0.897 gram of $Ni(CO_3)\cdot nH_2O$, 0.04 gram of $Co(CO_3)\cdot nH_2O$ and 0.062 gram of $Fe(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 425 °C with a ramp temperature of 6.7 ºc/min for 60 min and maintained at that temperature for 6 hours.

$Co_{45}Ni_{45}Fe_{10}N_x$

To obtain this material, 0.133 gram of $Fe(CO_3)\cdot nH_2O$, 0.479 gram of $Ni(CO_3)\cdot nH_2O$ and 0.389 gram of $Co(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 425 °C with a ramp temperature of 6.7 ºc/min for 60 min and maintained at that temperature for 6 hours. The material was characterized by PXRD as in Fig. 8 and HRTEM/EELS Fig 9.

$Co_{57}Ni_{14}Fe_{29}N_x$

To obtain this material, 0.929 gram of $Fe(CO_3)\cdot nH_2O$ and 0.371 gram of $Ni(CO_3)\cdot nH_2O$ and 1.200gram of $Co(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 425 °C with a ramp temperature of 6.7 ºc/min for 60 min and maintained at that temperature for 6 hours. The material was characterized by PXRD as in Fig. 10.

$Co_{90}Fe_5Ni_5N_x$

To obtain this material, 0.867 gram of $Co(CO_3)\cdot nH_2O$ and 0.074 gram of $Fe(CO_3)\cdot nH_2O$ and 0.059 gram of $Ni(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 425 °C with a ramp temperature of 6.7 ºc/min for 60 min and maintained at that temperature for 6 hours.

$\underline{Co_{90}Ni_{3.3}Fe_{3.3}Mn_{3.3}N_x}$

To obtain this material, 0.049 gram of $Fe(CO_3)\cdot nH_2O$ and 0.039 gram of $Ni(CO_3)\cdot nH_2O$ and 0.87 gram of $Co(CO_3)\cdot nH_2O$and 0.042 gram of $Mn(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 420 °C with a ramp temperature of 6.6 ºc/min for 60 min and maintained at that temperature for 6 hours. The material was characterized by PXRD as in Fig. 11.

$\underline{Ni_{99}Co_{0.3}Fe_{0.3}Mn_{0.3}N_x}$

To obtain this material, 1.981 gram of $Ni(CO_3)\cdot nH_2O$ and 0.005 gram of $Co(CO_3)\cdot nH_2O$ and 0.007 gram of $Fe(CO_3)\cdot nH_2O$and 0.006 gram of $Mn(CO_3)\cdot nH_2O$ grinded and mixed was placed in a ceramic holder. With a NH_3 flow rate of 100 mL/min the sample was heated to 420 °C with a ramp temperature of 6.6 ºc/min for 60 min and maintained at that temperature for 6 hours.

Example 2:

Example of characterization and use of nitrides as an OER catalyst.

Catalyst inks were prepared by grinding 60 mg of the desired catalyst with 270 µL of KOH-activated FAA-3 ionomer (5% w:w in EtOH) in a mortar and pestle (resulting in dried inks that contained 18% wt:wt FAA-3). Next, the catalyst/ionomer mixture was added to a scintillation vial with 6 mL of a 3:1 isopropanol/water solution and sonicated for 1 hour. The catalyst ink was then sprayed using an airbrush onto three pre-weighed Ni foil (purchased form Goodfellow), which were masked using kapton tape to expose 1 cm2 surface area on a hotplate set to 80 °C. The electrodes were then weighed after cooling to room temperature to determine the actual catalyst mass loading (0.9-1.1 mg/cm^2).

For each electrode, electrochemical impedance spectroscopy was conducted and the uncompensated series resistance (R_u) of the electrochemical system was determined using the high frequency point that intercepts the real axis of the Nyquist plot (typically 0.8-1.2 Ω). Cyclic voltammetry was then conducted from the open circuit potential of the electrode to

1.0 V vs Hg/HgO at a scan rate of 10 mV/s, back to 0.0 V vs Hg/HgO. The iR_u-corrected cyclic voltammogram of CoN_x, NiN_x, FeN_x, $Co_{45}Ni_{45}Fe_{10}N_x$, $Co_{57}Ni_{14}Fe_{29}N_x$, obtained as described in example 1, in comparison with state-of-the-art catalysts $NiCoFeO_x$ and commercially available IrO_x is presented in Figure 11. Notably, the mixed metal nitrides $Co_{45}Ni_{45}Fe_{10}N_x$, $Co_{57}Ni_{14}Fe_{29}N_x$ of example 1 are significantly outperform the pure metal nitrides, state-of-the-art $NiCoFeO_x$, and are comparable/better than IrO_x.

Example 3

Membrane electrode assemblies (MEAs) of $Co_{45}Ni_{45}Fe_{10}N_x$ of example 1.

A set of membrane electrode assemblies (MEAs) were constructed using IrO_x, $NiCoFeO_x$ and $Co_{45}Ni_{45}Fe_{10}N_x$ as OER catalysts and 0.5 mg/cm^2 PtC 60% on carbon cloth as hydrogen evolution reaction (HER) catalyst with a FAA-3-PK-75 membrane. Figure 13 and 14 shows the linear sweep voltammetry curves, and chronoamperometry, respectively, of the three membrane electrode assemblies (MEAs) in alkaline anion exchange membrane electrolysis. IrO_x and $NiCoFeO_x$ have a current density of approximately 400 mA/cm^2 at an applied cell voltage of 2.0V, similar to reported MEAs made with $NiCoFeO_x$ albeit under somewhat different conditions (nanopure water, 50 °C, with the catalyst sprayed onto the GDE). Meanwhile, the novel $Co_{45}Ni_{45}Fe_{10}N_x$ shows approximately 900 mA/cm^2 at the same applied potential, *more than double the current density*.

CLAIMS

1. A method of synthesis of transition metal nitrides characterized in that comprising the following steps:
   a) providing at least one precursor transition metal salts $M_x(A)_z$, wherein:
   the transition metal M is selected from Ni, Co, Fe, Cr, Ga, Al, Ti, Zn, Mn and any combination thereof, preferably from Fe, Ni, Co, Mn and any combination thereof;
   A is CO_3^{2-} or $CH_3CO_2^-$;
   wherein x is 1 or 2; and wherein z is the valence or mixed valences of the transition metal of the chosen precursor;
   with a ratio according to the expected stoichiometry of the metal or metals in the transition metal nitride;
   b) grinding the transition metal salts; and
   c) heating with a ramp temperature of between 8.75 ºC/min and 20ºC/min for a time of between 40 min and 70 min up to reach an annealing temperature of between 350 and 1200 °C the grinded transition metal salt of step (b) with NH_3 for nitridation at the annealing temperature for a period between 1 and 24 hours, and preferably for a period between 2 and 10 hours.

2. The method according to claim 1 wherein the heating of step (c) takes place under a flow of NH_3 for nitridation with a flow rate between 50 and 1000 mL/min, and preferably between 50 and 100 mL/min.

3. The method according to any of the claims 1 to 2, wherein in the step (a) at least two different precursors transition metal salts are provided.

4. The method according to claim 3, wherein the step (b) further comprising a pre-mixing of the selected salts before the griding.

5. The method according to any of the claims 1 to 4 wherein two different precursor transition metal salts M(A) of step (a) are used with a ratio according to the expected stoichiometry of the metals in the transition metal nitride to form binary transition metal nitrides.

6. A method of synthesis of transition metal nitrides according to claim 1 to 4 wherein three or four different precursor transition metal salts M(A) of step (a) are used with a ratio according to the expected stoichiometry of the metals in the transition metal nitride to form ternary or quaternary transition metal nitrides.

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7. Transition metal nitrides obtained by the method according to any of claims 1 to 6 wherein the nitride is $Co_{45}Ni_{45}Fe_{10}N_x$, $Ni_{60}Co_{30}Fe_{10}N_x$, $Ni_{33}Co_{33}Fe_{33}N_x$, $Ni_{90}Co_5Fe_5N_x$, $Co_{90}Fe_5Ni_5N_x$, $Co_{57}Ni_{14}Fe_{29}N_x$, $Ni_{99}Co_{0.3}Fe_{0.3}Mn_{0.3}N_x$, or $Co_{90}Ni_{3.3}Fe_{3.3}Mn_{3.3}N_x$, preferably multi transition metal nitride is $Co_{45}Ni_{45}Fe_{10}N_x$.

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8. The use of the transition metal nitrides according to claim 7 as a catalyst for the oxygen evolution reaction.

FIGURES

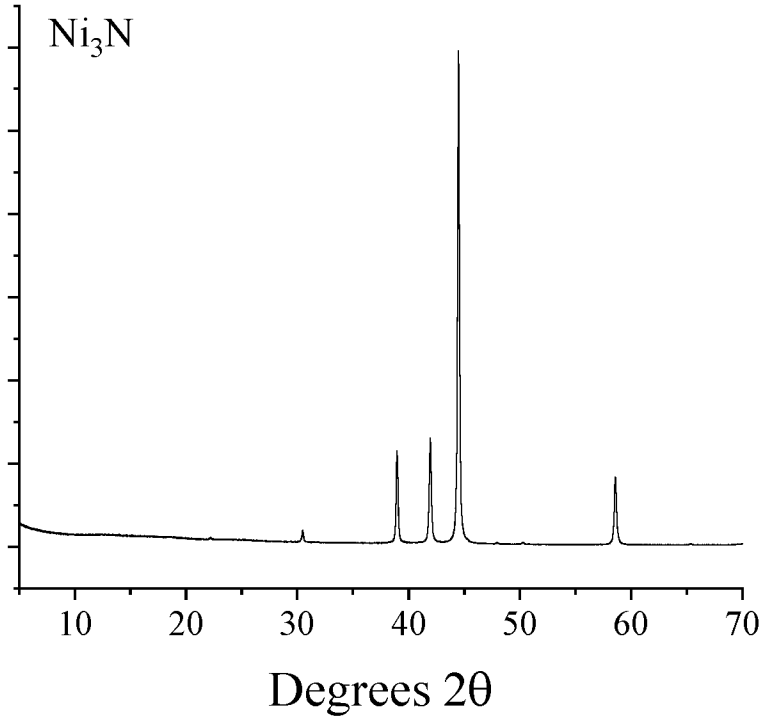

Fig. 1

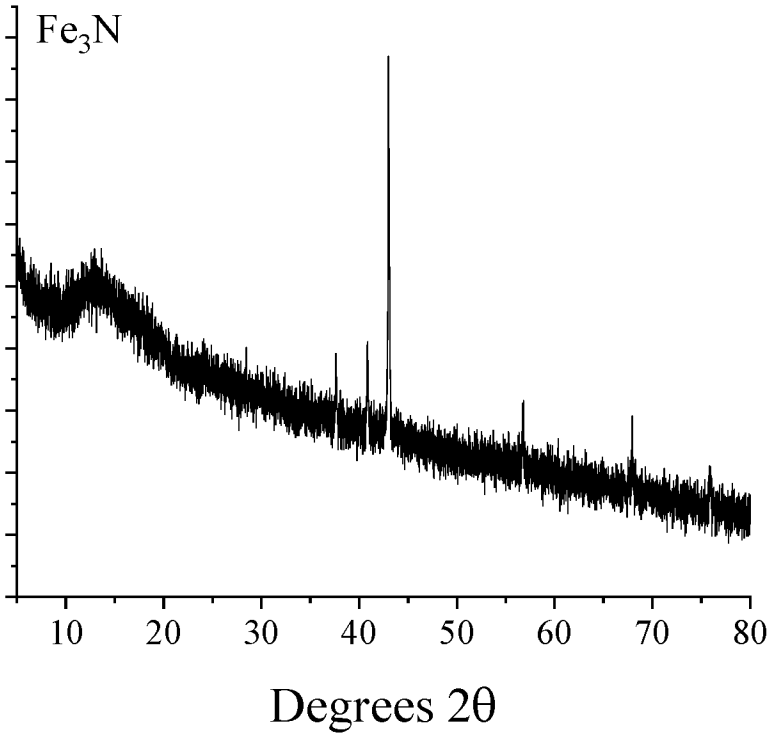

Fig. 2

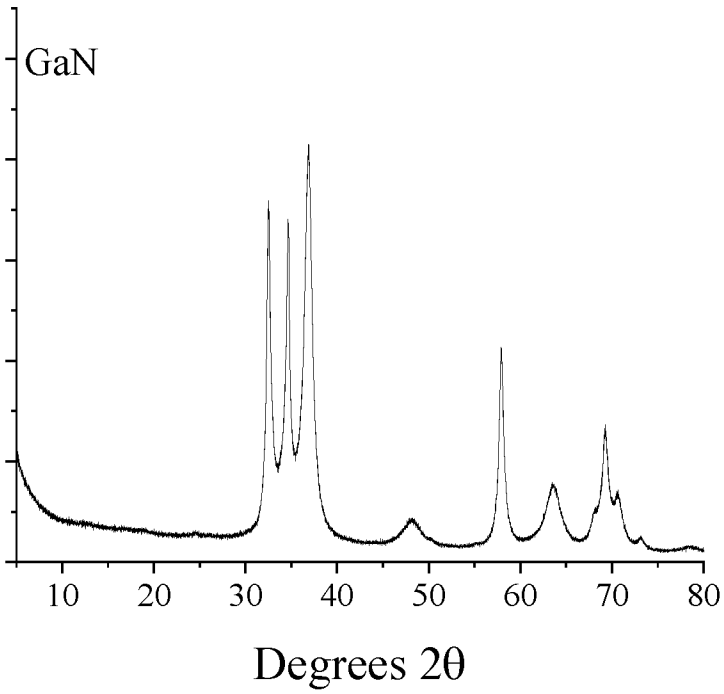

Fig. 3

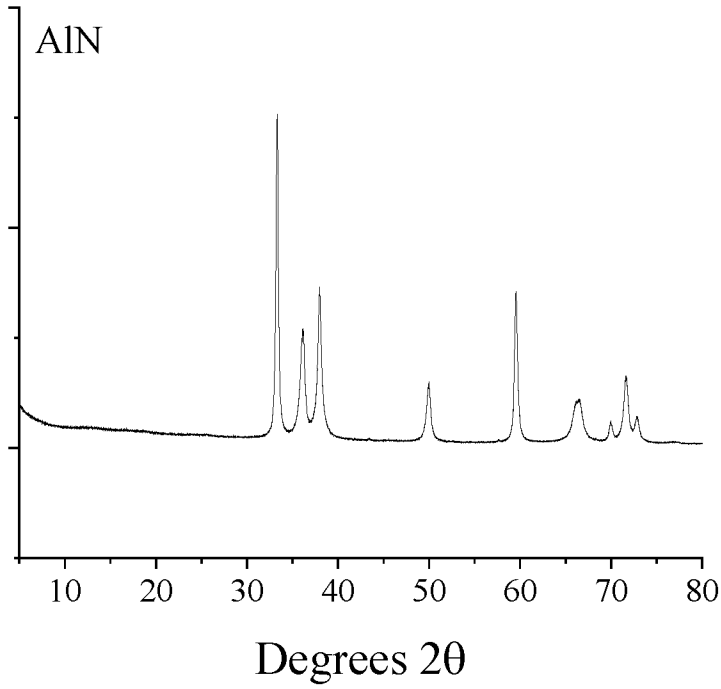

Fig. 4

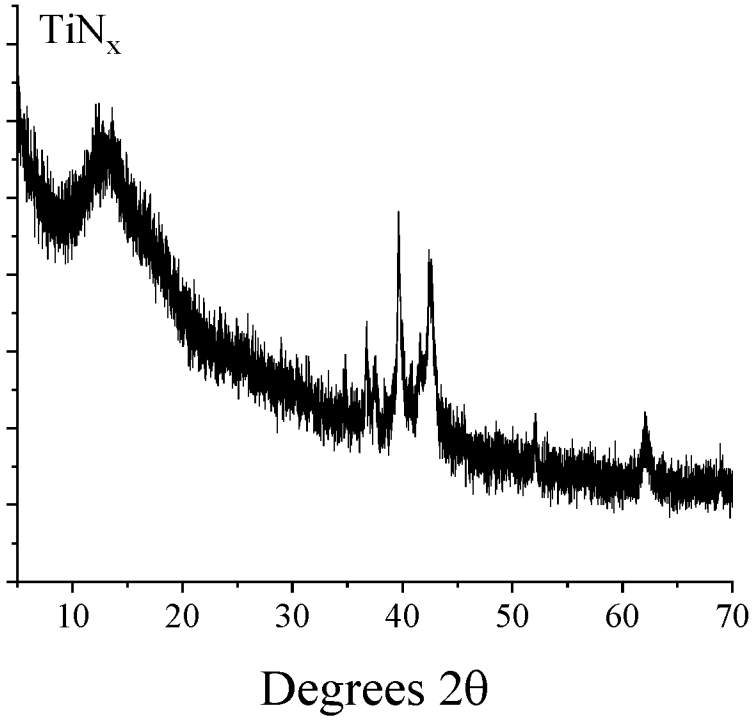

Fig. 5

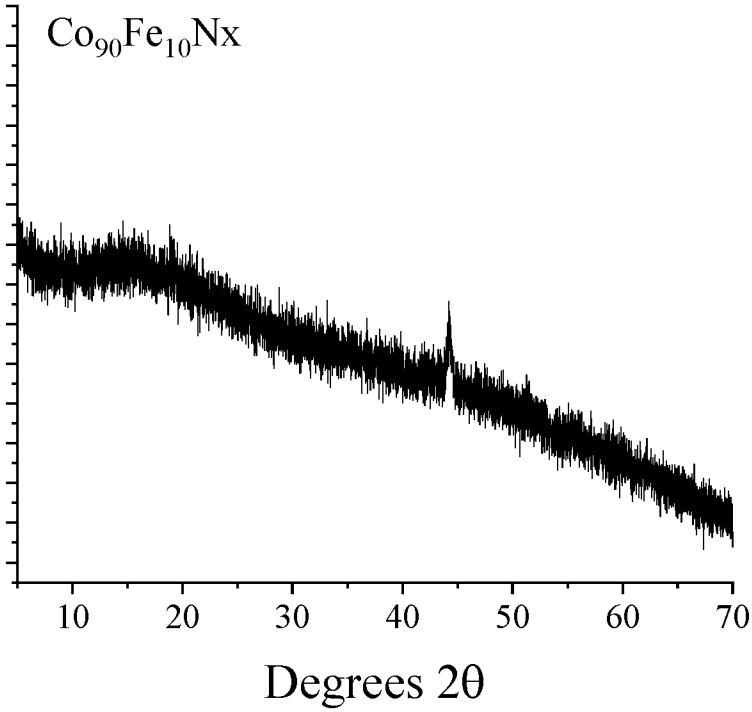

Fig. 6

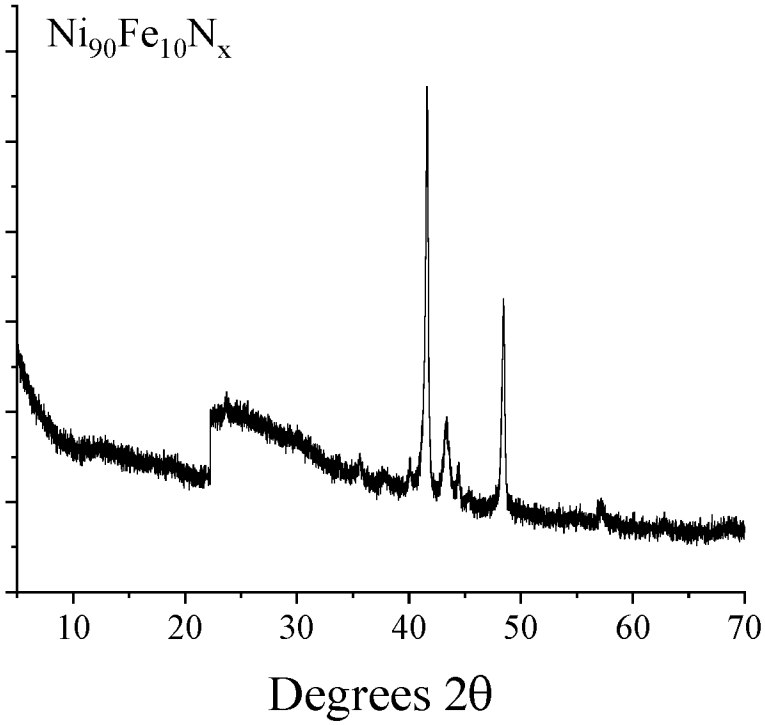

Fig. 7

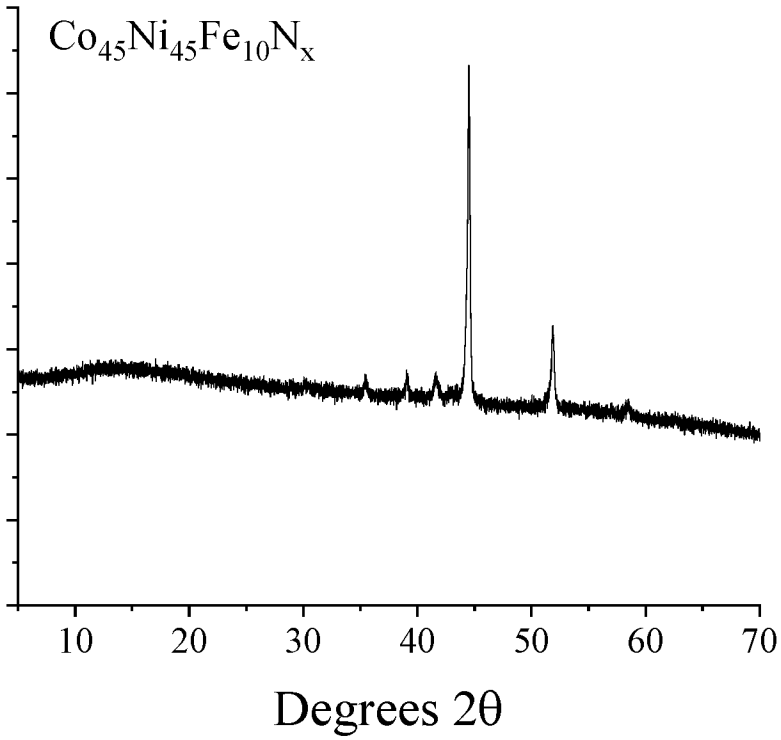

Fig. 8

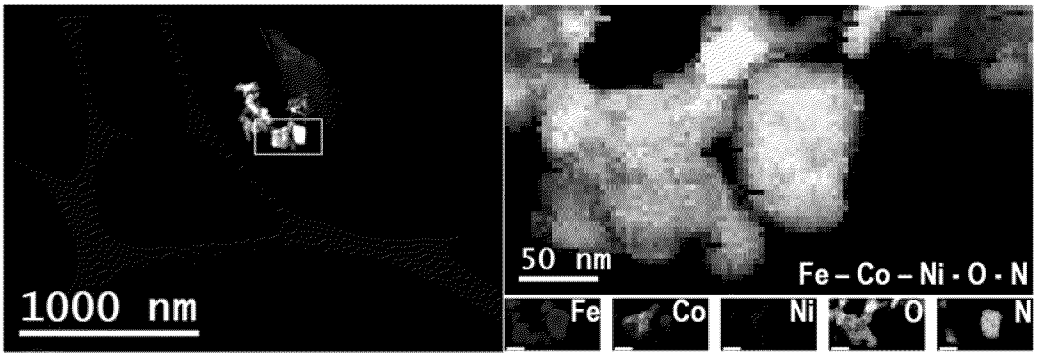

Fig. 9

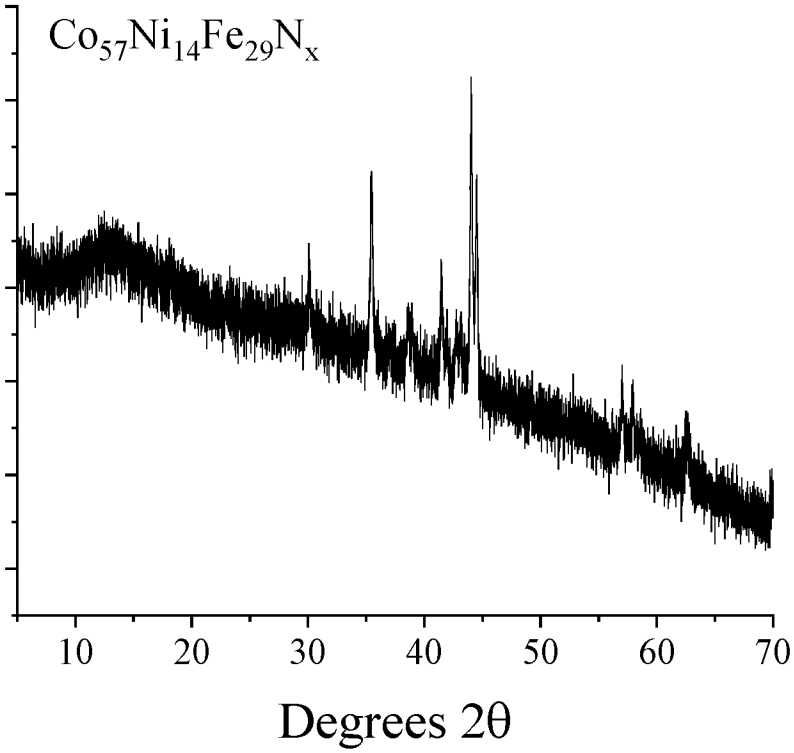

Fig. 10

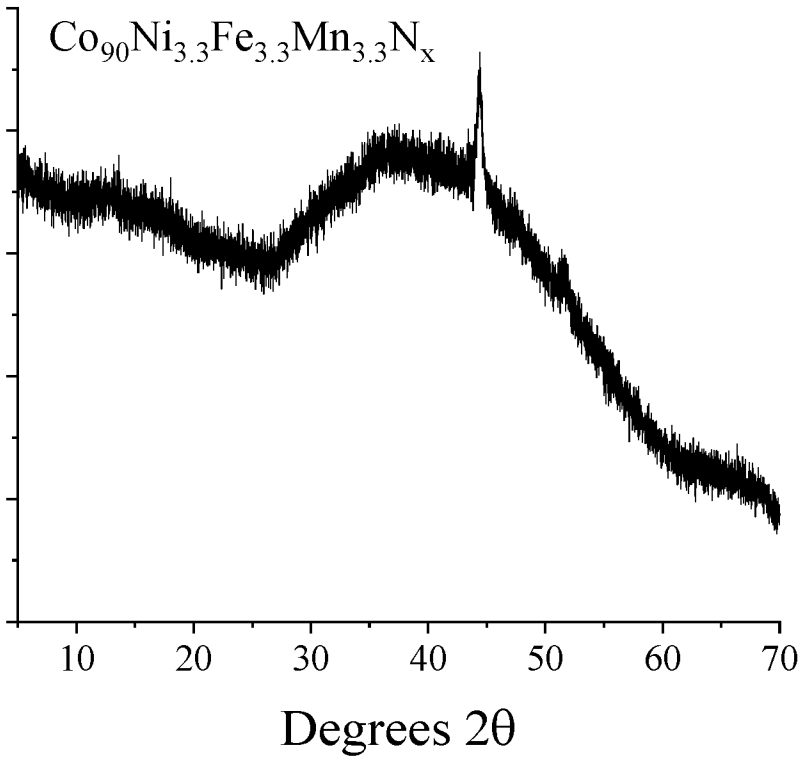

Fig. 11

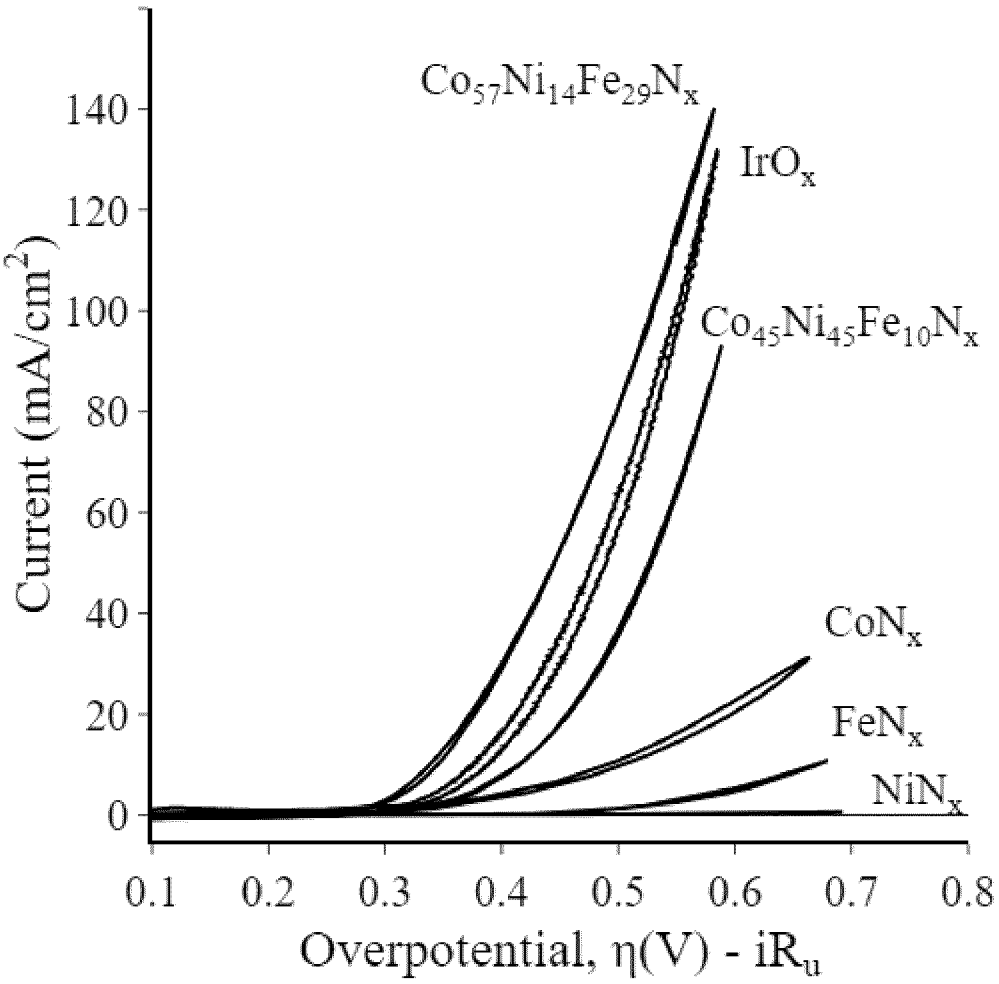
Co57Ni14Fe29Nx
IrOx
Co45Ni45Fe10Nx
CoNx
FeNx
NiNx
Current (mA/cm2)
0
20
40
60
80
100
120
140
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Overpotential, η(V) - iRu

Fig. 12

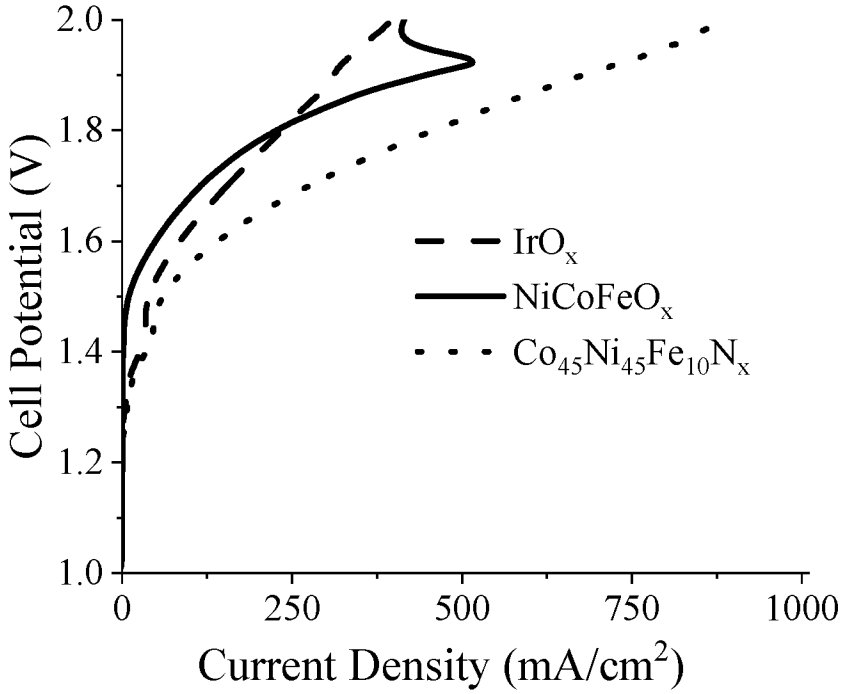
2.0
1.8
1.6
1.4
1.2
1.0
Cell Potential (V)
0
250
500
750
1000
Current Density (mA/cm^2)
IrO_x
$NiCoFeO_x$
$Co_{45}Ni_{45}Fe_{10}N_x$

Fig. 13

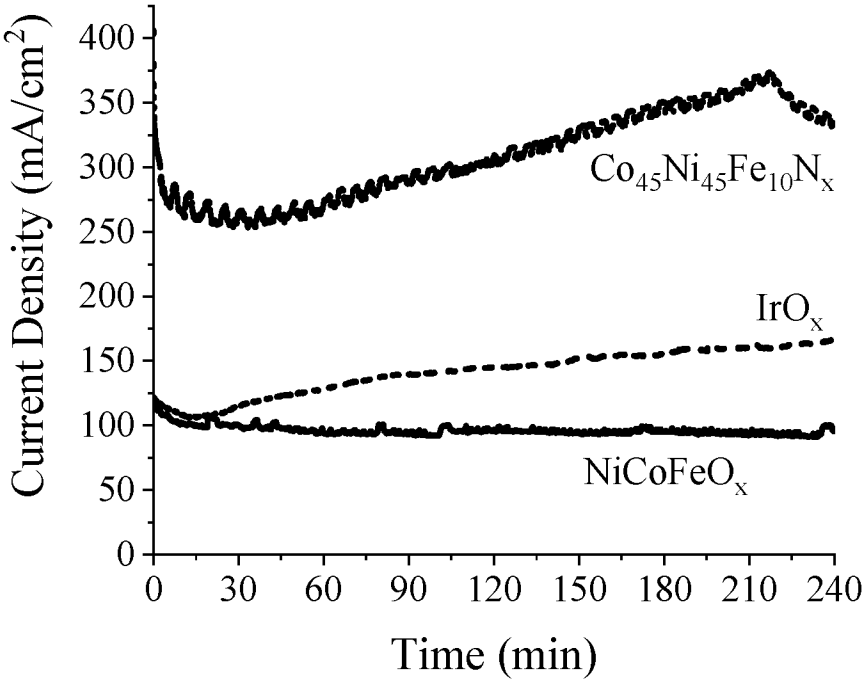
Current Density (mA/cm^2)
400
350
300
250
200
150
100
50
0
0
30
60
90
120
150
180
210
240
Time (min)
$Co_{45}Ni_{45}Fe_{10}N_x$
IrO_x
$NiCoFeO_x$

Fig. 14

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/066249

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B21/06 B01J27/24 B01J37/08 C01B21/072
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YUAN WENYU ET AL: "Interfacial Engineering of Cobalt Nitrides and Mesoporous Nitrogen-Doped Carbon: Toward Efficient Overall Water-Splitting Activity with Enhanced Charge-Transfer Efficiency", ACS ENERGY LETTERS, vol. 5, no. 3, 5 February 2020 (2020-02-05), pages 692-700, XP093097582, American Chemical Society ISSN: 2380-8195, DOI: 10.1021/acsenergylett.0c00116 abstract page 693, left-hand column, paragraph 2 - page 694, left-hand column, paragraph 1 -/--	1-8

[x] Further documents are listed in the continuation of Box C. [x] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 August 2024	18/09/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Sevillano Rodriguez

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	-& YUAN WENYU ET AL: "Supporting information - Interfacial Engineering of Cobalt Nitrides and Mesoporous Nitrogen-doped Carbon: Towards Efficient Overall Water Splitting Activity with Enhanced Charge Transfer Efficiency", ACS ENERGY LETTERS, vol. 5, 5 February 2020 (2020-02-05), pages 1-37, XP093097586, DOI: 10.1021/acsenergylett.0c00116 Retrieved from the Internet: URL:https://pubs.acs.org/doi/suppl/10.1021/acsenergylett.0c00116/suppl_file/nz0c00116_si_001.pdf> page S2, column 1 - page S3, column 1	
A	CN 112 058 299 A (UNIV SUN YAT SEN) 11 December 2020 (2020-12-11) claims 1-10; examples 1-7	1-8
A	LUO QIAO ET AL: "A review on the synthesis of transition metal nitride nanostructures and their energy related applications", GREEN ENERGY & ENVIRONMENT, vol. 8, no. 2, 1 April 2023 (2023-04-01), pages 406-437, XP093097651, ISSN: 2468-0257, DOI: 10.1016/j.gee.2022.07.002 page 406, left-hand column, paragraph 1 - page 407, right-hand column, paragraph 1	1-8
A	DONGIL A.B.: "Recent Progress on Transition Metal Nitrides Nanoparticles as Heterogeneous Catalysts", NANOMATERIALS, vol. 9, no. 8, 2 August 2019 (2019-08-02), page 1111, XP093097894, DOI: 10.3390/nano9081111 abstract page 1, paragraph 1 - page 2, paragraph 3	1-8

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/066249

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 112058299 A	11-12-2020	NONE	