Electrocatalysts for Efficient Water Electrolysis

The present invention relates to an electrocatalyst suitable for oxygen evolution in electrolytic processes, such as the electrolysis of water, comprising a perovskite-like double perovskite compound having the following general formula: $A_n (B'B')_{2n} O_{3n+1}$, wherein B represents Iridium, Ruthenium, Osmium, Rhenium, Rhodium, and/or combinations thereof, and to methods of its preparation and use.
Electrocatalysts for Efficient Water Electrolysis

The present invention relates to novel electrocatalysts for the electrolysis of water, their use, and to electrolytic cells and systems comprising the novel electrocatalyst materials.

Background of the Invention

Modern society and its energy demands are expanding at an unprecedented rate, whilst fossil fuel reserves dwindle and the carbon dioxide mediated greenhouse effect flourishes. These events are foundation to the recent heightened interest in renewable energy sources. Promising green energy candidates such as solar, wind, and hydro energy all have their energy generation decoupled from demand and as such require a way for storing excess energy.

Currently available means are not adequate for large scale long term energy storage due to a variety of reasons amongst which efficiency and cost are of most significance. One promising way of storing energy with high power density is the electrochemical formation of combustible or convertible fuels such as hydrogen (H₂) or hydrocarbons (CₓHᵧ).

However, the efficiency of many sustainable energy conversion and storage solutions, for instance metal-air batteries, fuel cells, or electrolyzers is inherently linked to, and limited by, the slow kinetics of the oxygen evolution reaction (further referred to herein as OER). Due to this, a high overpotential (η) is typically required to reach acceptable reaction rates, resulting in lower efficiency for these storage or energy conversion solutions. Water oxidation is the efficiency-limiting redox reaction of water electrolysis, and corresponds to the conversion according to the following formula: \(2 \cdot H₂O \rightarrow 4 \cdot H^+ + 4 \cdot e^- + O₂\). Water oxidation may provide a particularly good access to protons (H\(^+\)) and electrons (e\(^-\)) required for the storage or energy conversion solutions, as water is in abundance.

Generally, under conditions typical for water oxidation, i.e. at a potential of above 1.23 V vs. RHE, the majority of metallic surfaces acting as electrocatalysts will be covered by a metal oxide layer.

Presently used catalysts for water oxidation typically comprise precious metal oxides, such as IrO₂ or RuO₂. These catalysts, while typically offering an acceptable overpotential, are based on very rare resources and therefore quite expensive. Hence, the majority of research in recent years has focused on metal oxides of more
abundant and cheaper 3rd row transition metals instead of the highly active precious metals, such as iridium and ruthenium.

Due to the inherent chemical instability of these metal ions, alkaline media are strongly favoured, as so far only under such conditions, suitable chemical stability and prolonged catalyst lifetime could be ensured. In acidic media, however, the 3rd row transition metal catalysts are highly unstable, and hence not useful as replacement for RuO₂ and IrO₂.

An electrocatalyst system has now surprisingly been found that has a strongly enhanced activity, is stable and in an acidic environment, and when compared to the RuO₂ and IrO₂ electrocatalysts described above, has a strongly reduced precious metal content.

**Summary of the Invention**

Accordingly, in a first aspect, the present invention pertains to an electrocatalyst suitable for oxygen evolution in electrolytic processes, comprising a perovskite-like compound having the following general formula: $A_{n+1}(BB')_{n/2}O_{3n+1}$, wherein B represents Iridium, Ruthenium, Osmium, Rhenium, Rhodium, and/or combinations thereof.

In a second aspect, the present invention also relates to the preparation of electrocatalysts according to the present invention. Accordingly, the present invention relates to a method for the production of an electrocatalyst material, the method comprising:

(a) providing a mixture of suitable precursor metal salts in a particle size and form suitable for the preparation;

(b) subjecting the mixture to a temperature in the range of from 850°C to 950°C for a suitable period, preferably at least 2 hours, and

(c) sintering the resultant powder at a temperature in the range of from 1200°C to 1300°C, preferably 1225°C to 1275 °C, for a suitable period, preferably at least 48 hours, optionally accompanied by frequent intermittent regrinding, and

(d) furnace-cooling the obtained samples to room temperature. In a third aspect, the present invention also relates to systems comprising the electrocatalysts according to the present invention.
In an alternative method, the preparation of the electrocatalysts comprises

(i) the preparation of a first solution containing the precursor of the materials, and

(ii) depositing the material precursor from the solution onto a metal substrate by an induced solubility change, and

(iii) subjecting the thus formed deposited substrate to a thermal treatment at a temperature in the range of from 300 °C to 1300 °C, wherein the material exhibiting at least in part a double perovskite structure is formed.

In a fourth aspect, the present invention also relates to the use of the electrocatalysts according to the present invention in electrolysis reactions, preferably for the oxidation of water, or as catalytic electrocatalyst material in solid/air cells or batteries.

The present electrocatalyst materials preferably comprises a perovskite-like double perovskite having the stoichiometric formula $A_{n+1}(BB')_{n/2}O_{3n+1}$.

Without wishing to be bound to any particular theory, the three-dimensional arrangement of corner-share octahedra resulted in both in unprecedented catalytic activity and stability.

The double perovskite structure is closely related to the perovskite structure. The generic formula for a perovskite is $ABO_3$, where $A$ is a large cation and $B$ a smaller cation. Due to the difference in size, the coordination number for the A-cation is different than for the B-cation. In the case of a double perovskite, there are two similar cations on the B-site in a 1:1 ratio, resulting in $AB_{0.5}B'_{0.5}O_3$, or the generic form: $A_2BB'O_6$.

Many quaternary oxides with the general formula $A_2BB'O_6$ belong to the ordered double perovskites. Depending on the tolerance factor, $t = (r_A + r_O)/(2(r_{B,B} + r_O))$, where $r_{B,B}$ is the averaged ionic radii of B and B'-cations, the structure of double perovskites is either cubic ($t=1$), with the lattice parameter double of that of the primitive cubic perovskite and the space group $Fm\overline{3}m$, or distorted ($t>1$ or $t < 1$) with lower symmetry. This type of ordering of B and B' is also referred to as the rock-salt sublattice. Due to the difference in ionic radii between B and B', the structure may preferably attain the order as depicted in Figure 1. The double perovskite according to this invention preferably comprise alkaline earth metal ions to occupy the A-site,
while transition metals tend to occupy the B-site. However, this is by no means absolute, with many different combinations of A and B cations known.

Preferably, A represents = (AA')/2, wherein A and A' each independently may represents a metal ion selected from alkali or earth alkali metals. Preferred earth alkali metal ions comprise Ba, Sr, and Ca, with a preference for Ba or Sr, most preferred being Sr due to the good results obtained therewith.

In the formula, B represents Iridium, Ruthenium, Osmium, Rhenium, Rhodium, and/or combinations thereof. Preferably, B represents a metal ion selected from Iridium, Ruthenium, or combinations thereof, the most preferred being Iridium.

Preferably, B' represents a metal ion selected selected from one or more rare earth metals such as lanthanides or actinides. Preferred are lanthanides such as La, Ce, Pr, Nd, Tb, Y, or Lu. More preferred are Cerium, Neodymium, Prasodinium, Lanthanum, and/or Lutetium. Most preferred, these ions are preferably at the 3⁺ or 4⁺ oxidation stage.

Preferably, each B' atom is arranged in an octahedral oxygen coordination. In this way, the electrocatalyst comprises at least in part a layered perovskite crystalline structure, or a double perovskite crystalline structure comprising at least corner-shared octahedral oxygen coordination. It was found that layered structures, but preferably fully crystalline compounds with double perovskite structure resulted in both in unprecedented catalytic activity and stability.

Preferably, the electrocatalyst according to the invention is selected from the group comprising Ba₂CeIrO₆, Ba₂NdIrO₆, Ba₂TbIrO₆ and Sr₂YIrO₆, Ba₂YIrO₆, Sr₂IrO₄, or a combination thereof, due to the high activity in acidic media, and the low amount of iridium present in the material. Particularly preferred double perovskites include Ba₂PrIrO₆ (containing Ir⁴⁺); Ba₂NdIrO₆ (containing Ir⁵⁺); Ba₂YIrO₆ (containing a non-lanthanide at the B-site) and Sr₂YIrO₆ (containing strontium at the A-site).

Advantageously, the electrocatalyst further comprises a metal substrate, and an external catalytic layer comprising the electrocatalyst material. Any suitable metal substrate may be employed. Typically, Ti or Pb substrates are employed due to their inherent stability and easy availability. The electrocatalyst layer can advantageously be applied as set out herein below.

Short Description of the Figures

In Figure 1 the schematic representation of a generic A₂BB'O₆ double perovskite is depicted.
Figure 2 discloses the Ohmic drop corrected specific activity (j) of commercial IrO$_2$ and IrO$_2$ NPs (Nanoparticles) as a function of potential in 0.1 M HClO$_4$ saturated with air. Data points are acquired via controlled-potential chronoamperometric steps, whilst rotating at 1500 rpm. Error bars represent the standard deviations of at least three independent measurements. Catalyst loading was equal to 14.3 $\mu$g$_{oxide}$/cm$^2$ disk, whilst for IrO$_2$ NPs a mass loading could not be determined.

Figure 3 illustrates the Ohmic drop corrected specific activity (j) of commercial IrO$_2$, IrO$_2$ NPs, and Ba$_2$LnIrO$_6$ (Ln = La, Ce, Pr, Nd, Tb) as a function of potential in 0.1 M HClO$_4$ saturated with air. Data points are acquired via controlled-potential chronoamperometric steps, whilst rotating at 1500 rpm. Error bars represent the standard deviations of at least three independent measurements. Catalyst loading for plotted compounds was equal to 14.3 $\mu$g$_{oxide}$/cm$^2$ disk.

Figure 4 discloses the Ohmic drop corrected mass activity (i) of commercial IrO$_2$, IrO$_2$ NPs (from Lee et al.9), and Ba$_2$LnIrO$_6$ (Ln = La, Ce, Pr, Nd, Tb) as a function of potential in 0.1 M HClO$_4$ saturated with air. Data points are acquired via controlled-potential chronoamperometric steps, whilst rotating at 1500 rpm. Error bars represent the standard deviations of at least three independent measurements. Catalyst loading for plotted compounds was equal to 14.3 $\mu$g$_{oxide}$/cm$^2$ disk.

Figure 5 discloses the Ohmic drop corrected specific activity (j) of commercial IrO$_2$, IrO$_2$ NPs, Ba$_2$PrIrO$_6$, Ba$_2$YIrO$_6$ and Sr$_2$YIrO$_6$ as a function of potential in 0.1 M HClO$_4$ saturated with air, to allow for comparison between compounds of the invention with known compounds of differing Iridium levels. Data points are acquired via controlled-potential chrono-amperometric steps, whilst rotating at 1500 rpm. Error bars represent the standard deviations of at least three independent measurements. Catalyst loading for plotted compounds was equal to 14.3 $\mu$g$_{oxide}$/cm$^2$ disk.

Figure 6 discloses the Ohmic drop corrected specific activity (j) of Ba$_2$PrlrO$_6$ as a function of potential in 0.1M NaOH (pH 13), 0.001 M HClO$_4$ (pH 3), 0.01 M HClO$_4$ (pH 2) and 0.1 M HClO$_4$ (pH 1). The total concentration of perchlorate (ClO$_4$-) in each sample is held constant at 0.2 M. Data points are acquired via controlled potential chronoamperometric steps, whilst rotating at 1500 rpm. Error bars represent the standard deviations of at least three independent measurements, except in the case of pH 13, where only 1 sample was measured. Catalyst loading for plotted compounds was equal to 14.3 $\mu$g$_{oxide}$/cm$^2$ disk.

Figure 7 discloses the Observed and calculated profiles of SrTiO$_2$:Ir(25%) in the space group $Pm\bar{3}m$. Tick marks (I) indicate allowed reflections. Insert shows a close-up of the high 20 part. At the bottom, a difference curve ($k_{obs}$ - $k_{calc}$) is shown.
Figure 8 discloses the Ohmic drop corrected specific activity (j) of commercial IrO$_2$, IrO$_2$ NPs and SrTiO$_3$: Ir(25%) as a function of potential in 0.1 M HClO$_4$ saturated with air. Data points are acquired via cyclic voltammetry scanning at 10 mV/s, whilst rotating at 1500 rpm. Insert shows a close-up of the low specific current region. Catalyst loading for plotted compounds was equal to 71.5 $\mu$g$_{oxide}$/cm$^2$ disk. The oxidation peaks in the 1st scans at 1.5 V, correspond to the oxidation of the Au substrate.

Figure 9 discloses the observed and calculated profiles of Ba$_2$Pr(Nb$_{0.5}$Ir$_{0.5}$)O$_6$ for the space groups $Fm\overline{3}m$ and $I2/m$. Tick marks for Ba$_2$Pr(Nb$_{1-x}$Ir$_x$)O$_6$ and for Ba$_2$Pr(Nb$_{1-y}$Ir$_y$)O$_6$ indicate allowed reflections. Insert shows a close-up of the high 2θ part. At the bottom, a difference curve ($I_{obs}$ - $I_{cal}$) is shown.

Figure 10 discloses the observed and calculated profiles of Ba$_2$Pr(Ta$_{0.5}$Ir$_{0.5}$)O$_6$ in the space group $I2/m$. Tick marks indicate allowed reflections. Insert shows a close-up of the high 2θ part. At the

Figure 11 discloses the Ohmic drop corrected specific activity (j) of commercial IrO$_2$, IrO$_2$ NPs and Ba$_2$Pr(Ln$_{0.5}$Ir$_{0.5}$)O$_6$ (Ln = Ta, Nb) as a function of potential in 0.1 M HClO$_4$ saturated with air. Data points are acquired via cyclic voltammetry scanning at 10 mV/s, whilst rotating at 1500 rpm. Catalyst loading for plotted compounds was equal to 71.5 $\mu$g$_{oxide}$/cm$^2$ disk. The oxidation peaks in 1st scans at 1.5 V, correspond to the oxidation of the Au substrate.

Figure 12 discloses the Ohmic drop corrected specific activity (j) of Ba$_2$PrRuO$_6$ and Ba$_2$PrIrO$_6$ as a function of potential in 0.1 M HClO$_4$ saturated with air. Data points are acquired via cyclic voltammetry scanning at 10 mV/s, whilst rotating at 1500 rpm. Catalyst loading for Ba$_2$PrRuO$_6$ was 14.3 $\mu$g$_{oxide}$/cm$^2$ disk, whilst the loading for Ba$_2$PrIrO$_6$ was 15.1 $\mu$g$_{oxide}$/cm$^2$ disk.

Figure 13 discloses the Ohmic drop corrected specific activity (j) of Ba$_2$PrIrO$_6$ as a function of potential in 0.1 M MOH (M = Li, Na, K, Rb, Cs). Data points are acquired via controlled-potential chronoamperometric steps, whilst rotating at 1500 rpm. Error bars represent the standard deviations of at least three independent measurements, except in the case of NaOH, where they represent two independent measurements. Insert shows a Tafel plot close up of onset region. Catalyst loading for plotted compounds was equal to 71.5 $\mu$g$_{oxide}$/cm$^2$ disk.

Figure 14 discloses the Ohmic drop corrected specific activity (j) of commercial IrO$_2$, IrO$_2$ NPs and Ba$_2$PrIrO$_6$ as a function of potential in 0.1 M HClO$_4$, together with Ba$_2$PrIrO$_6$ in 0.1 M RbOH. Data points are acquired via controlled-potential chronoamperometric steps, whilst rotating at 1500 rpm. Error bars represent the standard deviations of at least three independent measurements. Catalyst loading for plotted
compounds was equal to 14.3 $\mu$g oxide / cm² disk, except in the case of Ba$_2$PrIrO$_6$ where it was 71.5 $\mu$g oxide / cm² disk.

Figure 15 discloses the Ohmic drop corrected specific activity ($\gamma$) of commercial IrO$_2$, IrO$_2$ NPs, Ba$_2$PrIrO$_6$, Sr$_2$IrO$_4$, and Pr$_5$IrO$_7$ as a function of potential in 0.1 M HClO$_4$. Data points are acquired via controlled-potential chronoamperometric steps, whilst rotating at 1500 rpm. Error bars represent the standard deviations of at least three independent measurements, except in the case of Sr$_2$IrO$_4$, where they represent two independent measurements. Catalyst loading for plotted compounds was equal to 14.3 $\mu$g oxide / cm² disk. The results indicate that at least a two-dimensional perovskite layer is suitably present.

**Detailed Description of the Invention**

The present invention relates to the use of a perovskite–like or double perovskite material comprising iridium alongside with a number of other metals. Figure 1 shows a schematic representation of the crystal structure of a generic A$_2$BB’O$_6$ double perovskite, as visualized by the VESTA software, showing the BO$_6$ (dark shaded) and B’O$_6$ (light shaded) octahedra, oxygen anions (black), and A cations (dark grey). In this structure, iridium ions are typically surrounded by six oxygen ions in an octahedral fashion. Each of these iridium ions is surrounded by six B-site ions, also in an octahedral fashion, as illustrated in Figure 1. The structure may advantageously accommodate a wide range of ions in different valence states with little lattice deformation, allowing to leverage this versatility to fine tune parameters such as catalytic performance and catalyst electrochemical stability.

Applicants found that such iridium containing double perovskites according to the invention exhibit superior electrochemical activity, at an iridium content typically in the range of from 25 to 35 wt%, which is considerably lower than the 85 wt% present in IrO$_2$.

The double perovskite structure may advantageously be determined by any suitable means, including but not limited to X-ray crystallography on powder diffraction patterns, as set out herein below.

Electrocatalysts comprising the double perovskites according to the invention were found to exhibit a considerably higher intrinsic catalytic activity towards water oxidation in acidic media than the best catalysts reported for this reaction (IrO$_2$). Simultaneously, the iridium weight content in these materials is typically a factor 3 lower than in the respective oxide while the catalytic activity of the compound is at least 10 times higher than IrO$_2$, as illustrated by Figure 3.
In the structure set out above, A preferably represents an alkali or earth alkali metal, preferably Ba or Sr.

In the structure, B preferably represents a rare earth metal, preferably from the Lanthanides, such as La, Ce, Pr, Nd, Tb, and/or Y, or mixtures thereof.

Preferred materials include Ba$_2$CeIrO$_6$, Ba$_2$NdIrO$_6$, Ba$_2$TbIrO$_6$ and Sr$_2$YIrO$_6$.

Ba$_2$YIrO$_6$, Sr$_2$IrO$_4$, Pr$_3$IrO$_7$, SrTi$_{0.75}$Ln$_{0.25}$O$_3$, Ba$_2$PrTaO$_6$, Ln$_{0.5}$O$_6$ and Ba$_2$PrNd$_{0.5}$Ir$_{0.5}$O$_6$.

Applicants found that the materials are readily available, and can be prepared in various suitable ways, including solid state chemistry at high temperatures, but also by (co)-precipitation and calcination steps.

One method involves the following steps:

(a) providing a mixture of suitable precursor metal salts in a particle size and form suitable for the preparation;

(b) subjecting the mixture to a temperature in the range of from 850°C to 950°C for a suitable period, and

(c) sintering the resultant powder at a temperature in the range of from 1200°C to 1300°C, preferably 1225°C to 1275°C, for a suitable period of time, optionally accompanied by frequent intermittent regrinding, and

(d) furnace-cooling the obtained samples to room temperature. In a third aspect, the present invention also relates to systems comprising the electrocatalysts according to the present invention.

Step (a) may be performed by any suitable manner. Step (b) is performed by heating the mixture to the temperature for a suitable period of time, preferably for at least 2 hours. Step (c) then involves heating the thus obtained first heated mixture to sintering conditions. It may involve regrinding, while the heating is performed for a suitable time period. It was found that 48 hours generally resulted in good sintered materials. In step (d), the sintered materials are allowed to cool down slowly to room temperature, thereby avoiding any thermal shocks.

In an alternative method, the preparation of the electrocatalysts comprises

(i) the preparation of a first solution containing the precursor of the materials, and

(ii) depositing the material precursor from the solution onto a metal substrate by an induced solubility change, and
(iii) subjecting the thus formed deposited substrate to a thermal treatment at a
temperature in the range of from 300 °C to 1300 °C, wherein the material
exhibiting at least in part a double perovskite structure is formed.

This process involves the co-precipitation of materials, but may effectively directly
result in the desired coating, upon calcinations in step (iii).

The following, non-limiting examples illustrate an embodiment of the
invention.

Experimental part

Synthesis and characterization

Samples of Ba₂MIrO₆ (M = La, Ce, Pr, Nd, Tb, Y), Ba₂PrRuO₆ and Sr₂YIrO₆ were
synthesized using a standard solid-state reaction as described in Fu et al., Fu, W.T. and
D.J.W. Ijdo, Re-examination of the structure of Ba₂MIrO₆ (M = La, Y): space group
D.J.W. Ijdo, On the space group of the double perovskite Ba₂PrIrO₆. Journal of Solid
symmetry and structure of the double perovskites Ba₂(2)LnRuO₆ (Ln = La, Pr and Nd).

Samples of Ba₂PrIrO₆ were prepared from BaCO₃, Pr₀₅₁₁ and Ir metal in platinum
 crucibles using the standard solid-state reaction. The well-ground mixtures were first
reacted at 900 °C for a few hours. The resultant powders were then sintered at 1250 °C
for several days, accompanied by frequent intermittent regrinding, and finally the samples
were furnace-cooled to room temperature. All synthesis were carried out in air.

Ba₂CeIrO₆, Ba₂NdIrO₆, Ba₂TbIrO₆ and Sr₂YIrO₆ prepared in a fashion similar to
Ba₂YIrO₆, using the processes as disclosed by Fu et al., and described above.

IrO₂ nanoparticles (NPs) were synthesized as described by Zhao et al., Zhao,
Y.X., et al., A High Yield Synthesis of Ligand-Free Iridium Oxide Nanoparticles with High
Electrocatalytic Activity. Journal
of Physical Chemistry Letters, 2011. 2(5): p.402-406. IrO₂ was used as commercially
available from Aldrich, in 99.99% t.m.b., trace metals basis purity.

Samples of Sr₂IrO₄, Pr₂IrO₇, SrTi₁₀.₇Sr₀₂₅O₃, Ba₂PrTa₀₅Sr₀₅O₆ and Ba₂PrNb₀₅Sr₀₅O₆
were prepared
from Sr(NO₃)₂ (Acros organics, 99%), iridium metal (Johnson, Matthey & co.), Pr₀₅₁₁
(E PCMOLKsm, 99.9%), TiO₂ (Riedel-de Haën AG, 99.8%), BaO₂ (Cerac, 99%), Ta₂O₅ (Fluka) and Nb₂O₅
(Aldrich, 99.9% t.m.b) in alumina crucibles using the standard solid-state reaction.
The well ground mixtures were first reacted at 900°C for a few hours. Samples of SrIrO₄ and PrIrO₃ were then sintered at 1200°C for 8 hours. Samples of SrTi₀.₇₁Ir₀.₂₉O₃ were sintered for 18 hours at 1100 °C; followed by 36 hours at 1250 °C. Samples of Ba₂PrTa₀.₅₁Ir₀.₄₉O₉ and Ba₂PrNb₀.₅₁Ir₀.₄₉O₉ were sintered for 48 hours at 1250 °C; followed by 12 hours at 1350 °C; followed by 12 hours at 1450 °C. All samples were ground intermittently, and furnace-cooled to room temperature. All reactions were carried out in air.

X-ray powder diffraction patterns were collected on a Philips X'Pert diffractometer, equipped with the X'Celerator, using Cu-Kα radiation in steps of 0.020° (2θ) with 10 s counting time in the range 10° < 2θ < 100°. Calculations were performed by the Rietveld method, using the software Rietica. The profiles were fitted using a Pseudo-Voigt function, while the Chebyshev polynomial function with 12 parameters was used to fit the background.

Reagents: All electrolyte solutions were prepared by dissolving the appropriate amount of chemicals in 18.2 M_/cm water from Millipore Milli-Q. LiOH·H₂O (Aldrich, 99.95% t.m.b.), NaOH (Sigma-Aldrich, 99.99% t.m.b.), KOH (Sigma- Aldrich, 99.99% t.m.b.), RbOH solution (Aldrich, 99.9% t.m.b.), CsOH·H₂O (Aldrich, 99.95% t.m.b.), HClO₄ solution (Merck, EMSURE), HNO₃ solution (Sigma-Aldrich, ACS reagent grade), NaClO₄·H₂O (Fluka, 99% for HPLC), Nafion solution (Aldrich) and argon (purity grade 6.0) were used as received.

Na-exchanged Nafion. The immobilizing agent (Nafion) was ion-exchanged with sodium hydroxide to avoid possible corrosion of the oxide powders when mixed together. Nafion was mixed with a 0.05 M NaOH solution in a 1:1 volumetric ratio to yield near pH neutral ion-exchanged Nafion.

Electrocatalyst preparation. Catalyst inks were prepared by sonication (Bransonic 2510, Branson) of appropriate amounts of oxide catalyst, ion-exchanged Nafion and ethanol (Sigma-Aldrich, 99.8%) to yield inks with final concentrations of 1 mg_oxyde / 1 mL_{ink} or 5 mg_oxyde / 1 mL_{ink} and 0.7 mg_{Nafion} / 1 mL_{ink}. Next, 2.5 μL ink was drop-cast onto an Au electrode (0.17 cm² geometrical area) surrounded by a Pt ring, which was polished to a mirror finish with 0.04 μm alumina slurry (Kemet) on a polishing cloth (Buehler), and sonicated for 5 minutes prior to drop-casting. After drop-casting, the ethanol was evaporated under vacuum. The final catalyst loading was 14.3 μg_oxyde / cm² disk or 71.5 μg_oxyde / cm² disk, with 2.2 μg_{Nafion} / cm² disk.

Loading concentrations are specified for each graph shown. Prior to making catalyst inks, oxide powders were dry ground using a pestle and mortar to increase
homogeneity of the final inks. IrO$_2$ NPs could not be drop-cast due to resulting agglomeration issues when dried. Therefore, they were electrodeposited on the electrode directly from solution. The particles were electrodeposited via dipping the electrode in a mildly acidic solution of NPs (2 mM precursor), and applying a constant potential of 1.3 V vs. Ag/AgCl for 120 seconds.

Surface area determination: The electrochemically active surface was estimated from double-layer capacitance using cyclic voltammetry (CV). A 100 mV window where capacitive charging is the only source of current is verified, as the so called double-layer region. Then the CVs in this window, 0.8 – 0.9 V, at different scan rates, namely v = 0.025; 0.050; 0.075; 0.1; 0.15; 0.2; 0.3; 0.4 and 0.5 V/s. From the middle of the potential window one then extract the charging current ($i_c$) for each scan rate v.

These parameters are related to the double-layer capacitance ($\pi C$) via equation 1:

$$i_c = v \cdot \pi C,$$  \hspace{1cm} (1)

A plot of charging current versus scan rate should yield a straight line whose slope is equal to the double-layer capacitance. The double-layer capacitance is related to the electrochemically active surface area ($A_s$) via the specific capacitance ($C^*$) as exemplified in equation 2:

$$A_s = \frac{\pi C}{C^*},$$ \hspace{1cm} (2)

where $C^* = 60 \ \mu F/cm^2$ is used in this work, this refers to a theoretical value calculated for oxides in general, unrelated to crystal structure.

Different methods for determining surface area such as Brunauer–Emmett–Teller (BET), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) do exist, to name but a few important ones. However, the equipment necessary for these methods is not available to the authors, nor would they yield values closer to the ‘real’ active surface area, since they rely on particle size and related surface area prior to incorporation in thin-films. As such, the actual electrochemically active surface will be different as compared to surface areas determined via these methods.

Electrochemistry: Glassware was cleaned via boiling in a 3:1 mixture of sulfuric acid and nitric acid, and stored in permanganate solution between experiments. Prior to each experiment glassware was cleaned by boiling in Milli-Q water. Electrolyte solutions
were prepared by dissolving the appropriate amount of chemicals in 200 mL Milli-Q water. Where stated, the electrolyte was purged of oxygen by bubbling argon for 20 minutes, or saturated with air by bubbling with air for 20 minutes. Air was first bubbled through a 6 M KOH solution to remove impurities. All electrochemical measurements were carried out in a two compartment electrochemical cell with the reference electrode separated by a Luggin capillary. Measurements were performed using a rotator (Electrocraft Motomatic Motor Generator) to which the working electrode, loaded with thin-film catalyst, was attached. A gold wire was used as counter electrode. OER activities were obtained whilst rotating at 1500 rpm. A reversible hydrogen electrode (RHE) was employed as reference electrode, and potentials were controlled using a potentiostat/galvanostat (Autolab PGSTAT12). Electrocatalytic behaviour at room temperature was explored via cyclic voltammetry as well as via a series of controlled-potential chronoamperometric steps. In the latter, potential was held constant for 30 seconds and the steady-state measured current is plotted versus the applied potential.

Electrolyte resistance. The ohmic resistance of an electrochemical cell filled with electrolyte is given in equation 3:

$$R = \frac{1}{\kappa} \cdot \frac{l}{A}, \quad (3)$$

In this equation, $\kappa$ is the specific conductance of the electrolyte, while $l$· A$^{-1}$ can be considered a pseudoconstant of the set-up, dependant on the geometry, size, and spacing of the electrodes. To determine the constant l· A$^{-1}$ for the set-up used in this work, the resistance of the cell (filled with 0.1M HClO$_4$) was extracted from impedance spectra obtained by Electrochemical Impedance Spectroscopy (EIS) in the frequency range 50 kHz - 0.5 Hz at 0.8, 0.9 and 1.0 V vs. RHE. The specific conductance of the electrolyte was then measured using a MeterLab. Table 1 shows the obtained resistances for electrolyte solutions.
Table 1. Obtained resistances for electrolyte solutions.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Electrolyte resistance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation series:</td>
<td></td>
</tr>
<tr>
<td>0.1 M LiOH</td>
<td>53</td>
</tr>
<tr>
<td>0.1 M NaOH</td>
<td>49</td>
</tr>
<tr>
<td>0.1 M KOH</td>
<td>48</td>
</tr>
<tr>
<td>0.1 M RbOH</td>
<td>44</td>
</tr>
<tr>
<td>0.1 M CsOH</td>
<td>43</td>
</tr>
<tr>
<td>pH series:</td>
<td></td>
</tr>
<tr>
<td>0.1 M HClO₄ +</td>
<td>22</td>
</tr>
<tr>
<td>0.1 M NaClO₄</td>
<td></td>
</tr>
<tr>
<td>0.01 M HClO₄ +</td>
<td>48</td>
</tr>
<tr>
<td>0.19 M NaClO₄</td>
<td></td>
</tr>
<tr>
<td>0.001 M HClO₄ +</td>
<td>57</td>
</tr>
<tr>
<td>0.2 M NaClO₄</td>
<td></td>
</tr>
<tr>
<td>0.1M NaOH +</td>
<td>23</td>
</tr>
<tr>
<td>0.2M NaClO₄</td>
<td></td>
</tr>
</tbody>
</table>

Standard conditions:
0.1 M HClO₄ 24 ± 0.2*

*Average of 5 independent measurements. The actual pH was slightly lower than 1 at 0.94.

CDM230 conductivity meter: The constant I· A· cm⁻¹ was then determined to be 1.1

All resistances used in this work were obtained by measuring k and converting

to this the resistance. The obtained values for electrolyte resistances are listed in Table 1
and these are the values used when correcting for ohmic drop, where stated.

Detection of oxygen formation: A Rotating Ring Disk Electrode (RRDE) set-up
was used for determining the formation of oxygen. Briefly, cyclic voltammetry was
performed on the Au disk loaded with thin-film catalyst, whilst rotating at 1500 rpm. The
formed oxygen, if any, was then partially reduced back to water at the Pt ring surrounding
the disk, held at 0.45V vs. RHE (O₂ + 4· H⁺ + 4· e⁻ → H₂O). Therefore, a decrease in ring
current corresponds to the formation of oxygen at the disk.

Faradaic efficiency: The efficiency of Ba₃Pr₁IrO₈ was measured using the same
setup as described in the previous section; in a 0.1M HClO₄ solution purged with Ar. Ring
background currents were observed to be below 0.5 µA. To determine efficiency, one
needs to know the collection factor, which is defined as stated in equation 4 (for a
catalyst with 100% efficiency). For this equation to hold true, water is assumed to be
oxidized to oxygen on the disk, and oxygen is assumed to be reduced to water on the Pt ring:

\[ N = \frac{i_{\text{ring}}}{i_{\text{disk}}} \]  

(4)

Linear sweep voltammetry of IrO₂ NPs electrodeposited on the disk in the region 1.525 < E < 1.75 V vs. RHE, while keeping the ring constant at 0.4 V vs. RHE, was used to determine the collection factor. IrO₂ was used because its efficiency is known to be (very near) 100%. The calculated value for N was 0.20 ± 0.01. This value is in close agreement with the collection factor as calibrated with the [Fe(CN)₆]³⁻ / [Fe(CN)₆]⁴⁻ couple (N = 0.23). The slight difference between calculated collection factors may be attributed to the non-ideal outward flow of O₂.

The faradaic efficiency of Ba₂PrIrO₆ for OER was then determined by dropcasting 14.3 μg/cm² disk and doing linear sweep voltammetry in the potential window 1.25 < E < 1.75 V vs. RHE, while again keeping the ring at 0.4 V vs. RHE.

The efficiency was then calculated via equation 5:

\[ \omega = \frac{i_{\text{ring}}}{i_{\text{disk}} \cdot N} \]  

(5)

The calculated specific area at the used loading concentration is very similar to the electrode geometrical area. Due to the fact that the calculated specific area of the oxide and the geometrical area of the electrode are comparable, the faradaic efficiency was calculated for the potential window: 1.525 < E < 1.575 V vs. RHE, where the double perovskites generally show a current density of 1 mA/cm² oxide (see also Figure 3).

In this potential window, the faradaic efficiency of Ba₂PrIrO₆ for OER was determined to be 82.5 ± 13 %. The large error in this value is mainly due to the fact that oxygen bubbles tend to form very easily on the surface of these particular double perovskites, much more so than in the case of e.g. electrodeposited IrO₂ NPs. These bubbles trap part of the formed oxygen, resulting in bubble growth and lowering of the effective collection factor. As they reach a certain size, they will dissociate from the surface, but will not be detected on the ring as only dissolved oxygen is detected. This formation and subsequent release of oxygen bubbles yields a noisy ring response.

However, due to the fact that the used potential window is already very close to the onset potential (about 1.45 V vs. RHE), using a lower potential window would give rise to other difficulties, e.g. ring background current interference.
To illustrate relative activity of the compounds measured in this work, all data was compared to the catalytic activity of both commercial IrO$_2$ and freshly prepared IrO$_2$ nanoparticles (NPs), measured under the same conditions (Figure 2). Activity of commercially sourced iridium oxide was found to differ from that of a nanosized variant, despite both being normalized by surface area.

The nanoparticles presented in this work were prepared as exemplified by Zhao et al., Zhao, Y.X., et al., A High Yield Synthesis of Ligand-Free Iridium Oxide Nanoparticles with High Electrocatalytic Activity. Journal of Physical Chemistry Letters, 2011. 2(5): p. 402-406. However, they exhibit catalytic activity comparable to the nanoparticles of Lee et al., Synthesis and Activities of Rutile IrO$_2$ and RuO$_2$ Nanoparticles for Oxygen Evolution in Acid and Alkaline Solutions, Journal of Physical Chemistry Letters, 2012. 3(3): p. 399-404, even though those were synthesized via a different route. Activity of both variants of IrO$_2$ is added as a reference.

All double perovskites according to the invention, as shown in Figure 3, exhibit a higher intrinsic catalytic activity for water oxidation than commercial IrO$_2$ and IrO$_2$ NPs.

Neither the cation present at the B-site, nor the oxidation state of iridium seems to significantly affect catalytic activity (i.e. their error bars overlap). Particularly high catalytic activity was found for a preferred double perovskite containing neodymium on the B-site, which exhibits higher catalytic activity than all other double perovskites.

However, the catalytic activity for all plotted compounds is at least one order of magnitude higher than that of commercial and nanosized IrO$_2$. As such, the cation residing on the A- and/or B-site seems not to be the crucial component for the improved catalytic performance with respect to (nanosized) IrO$_2$. The change in Tafel slope observed at high overpotentials appears to be caused by the formation and growth of bubbles on the surface, which adhere tightly to the surface, even at rotating speeds of 1500 rpm.

In Figure 4, the same compounds as shown in Figure 3 are depicted, only now normalized per gram of iridium.

For the internally prepared IrO$_2$ NPs as comparative examples, mass activity could not be calculated due to the way they were prepared and deposited. However, since they compare well to the nanoparticles reported by Lee et al., see also Figure 3, their data is added instead. Even though the double perovskites contain less iridium, the
difference in activity is a lot less pronounced in this plot, with some double perovskites even exhibiting comparable activity (e.g. Ba$_2$CeIrO$_6$). This is primarily due to the fact that nanoparticles exhibit an increased surface to weight ratio as compared to microsized particles, resulting in more active sites per unit mass and thus higher mass activity.

Effect of the A-site and non-lanthanides on the B-site: The effect of cations other than lanthanides on the B-site as well as the effect of the cation on the A-site was investigated via comparing Sr$_2$YIrO$_6$ and Ba$_2$YIrO$_6$. The measured catalytic activity of these two double perovskites is plotted in Figure 5. Ba$_2$PrIrO$_6$ is also plotted, together with, as comparative examples, commercial and nanosized IrO$_2$ as a reference.

Both compounds show catalytic behaviour comparable to that of Ba$_2$LnIrO$_6$-type double perovskites, despite not containing a lanthanide on the B-site (Ba$_2$YIrO$_6$) and/or barium on the A-site (Sr$_2$YIrO$_6$). These results indicate that the cation residing on the B-site does not necessarily have to be a lanthanide, and that A-site cation substitution may significantly affect catalytic activity, with Sr$_2$YIrO$_6$ showing higher intrinsic catalytic activity than Ba$_2$YIrO$_6$. However, as with the B-site cation, the cation present on the A-site appears not to be responsible for the large shift in activity as compared to IrO$_2$.

Interestingly, though Sr$_2$YIrO$_6$ shows higher catalytic activity than Ba$_2$YIrO$_6$, the latter proves to be more stable, see also Table 2. Electrochemical stability of double perovskites: Short term electrochemical stability for the compounds discussed so far was tested via cyclic voltammetry. Briefly, catalytic activity was measured via cyclic voltammetry in the region 1.25 – 1.8 V vs. RHE at a scan rate of 10 mV/s, before and after 500 cycles in the same potential window at 0.5 V/s.

Thereafter, the relative decrease in catalytic activity ($\Delta$) was calculated via equation 6:

$$\Delta = \frac{(j_{E \text{ max,} s1}^{\text{z1}} - j_{E \text{ max,} s1}^{\text{z1} \to 500})}{j_{E \text{ max,} s1}^{\text{z1}}}$$

wherein $j_{E \text{ max,} s1}^{\text{z1}}$ is the specific current at the highest ohmic drop corrected potential in the 1st scan, and $j_{E \text{ max,} s1}^{\text{z1} \to 500}$ wherein $j_{E \text{ max,} s1}^{\text{z1} \to 500}$ is the specific current at the same potential after 500 cycles.
In Table 2 this relative decrease in activity is given for commercial and nanosized \( \text{IrO}_2 \), together with a selection of double perovskites: \( \text{Ba}_2\text{PrIrO}_6 \) (containing \( \text{Ir}^{4+} \)); \( \text{Ba}_2\text{NdIrO}_6 \) (containing \( \text{Ir}^{5+} \)); \( \text{Ba}_2\text{YIrO}_6 \) (containing a nonlanthanide at the B-site) and \( \text{Sr}_2\text{YIrO}_6 \) (containing strontium at the A-site).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Decrease in activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{IrO}_2 ) (commercial)</td>
<td>74%</td>
</tr>
<tr>
<td>( \text{IrO}_2 ) NPs</td>
<td>81%</td>
</tr>
<tr>
<td>( \text{Ba}_2\text{PrIrO}_6 )</td>
<td>80%</td>
</tr>
<tr>
<td>( \text{Ba}_2\text{NdIrO}_6 )</td>
<td>42%</td>
</tr>
<tr>
<td>( \text{Ba}_2\text{YIrO}_6 )</td>
<td>17%</td>
</tr>
<tr>
<td>( \text{Sr}_2\text{YIrO}_6 )</td>
<td>76%</td>
</tr>
</tbody>
</table>

Table 2. Relative decrease in activity for \( \text{IrO}_2 \) and a selection of double perovskites.

It must be noted that this is quite a crude method for determining stability, with a number of factors that may not be primarily related to stability also affecting the outcome, e.g. possible film tearing, catalyst dissociation, and/or surface roughening/smoothing.

Yet, as conditions for each oxide were comparable, it is considered as a suitable indication of relative stability and how stability differs between samples.

As can be seen in Table 2, relative stability is actually highly variable between different double perovskites, with observed values ranging between 17% and 80%. The values obtained for \( \text{IrO}_2 \) however do not differ too much between commercial and nanosized \( \text{IrO}_2 \) at 74% vs. 81%.

To test electrochemical stability, a current of 0.25 A was passed through a cylindrical pellet of \( \text{Ba}_2\text{PrIrO}_6 \) with radius 6.5 mm and height 3 mm for 2 hours. This experiment was conducted in a two electrode set-up, where the potential was not controlled nor monitored, with the purpose of seeing which ions are most prone to dissolution. During the course of the experiment a purplish film was deposited at the cathode, which was separated from the electrolyte via centrifugation and dissolved in concentrated nitric acid, after which electrolyte and dissolved film were analyzed for dissolved metal species via Inductively Coupled Plasma (ICP).

The obtained results are summarized in Table 3:
Table 3. Double perovskite cation dissolution during water oxidation.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Relative concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrolyte:</strong></td>
<td></td>
</tr>
<tr>
<td>Iridium</td>
<td>1 (6.4 μM)</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>2150</td>
</tr>
<tr>
<td>Barium</td>
<td>9400</td>
</tr>
<tr>
<td><strong>Film deposit:</strong></td>
<td></td>
</tr>
<tr>
<td>Iridium</td>
<td>1 (10.4 μM)</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>1200</td>
</tr>
<tr>
<td>Barium</td>
<td>115</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td></td>
</tr>
<tr>
<td>Iridium</td>
<td>1 (16.8 μM)</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>1550</td>
</tr>
<tr>
<td>Barium</td>
<td>3650</td>
</tr>
</tbody>
</table>

As can be seen in Table 3, total barium (A-site cation) and praseodymium (B-site cation) concentrations exceed iridium (B'-site cation) concentrations by three orders of magnitude. This indicates that valuable iridium is lost only in small amounts during water oxidation, although activity does decrease with time (see Table 2). The ratio of dissolved barium vs. praseodymium is 2.35:1, which roughly resembles their ratio in the double perovskite structure (2:1). Therefore, preferably, to increase catalyst stability, as the most readily solvable ions can actually be replaced by other metal ions.

Effect of pH on catalytic activity. Catalytic activity was observed to be vastly different in alkaline media as compared to acidic media; therefore the effect of pH on catalytic activity was investigated, while keeping the ionic strength constant. A pH series consisting of pH 1, 2, 3 and 13 was prepared, where the concentration of perchlorate (ClO₄⁻) was kept constant at 0.2 M via the addition of appropriate amounts of NaClO₄. The catalytic activity of Ba₂PrIrO₆ under these conditions was measured, and the measured activities are plotted in Figure 6.

As can be seen in Figure 6, activity seems to increase with decreasing pH. However, further on in this work it is shown that cationic species affect catalytic activity in alkaline media. If such an effect is also present in acidic media, this increase in activity with decreasing values for pH could possibly be explained by the fact that Na-concentrations decrease with decreasing pH, as fewer NaClO₄ is needed to yield the same ionic strength. Values for pH lower than 1 were not measured, due to the fact that the solubility of perchlorate salts then comes into play.
Effect of B-/B'-site ordering on catalytic activity: Most double perovskites contain 
B- and B'-octahedra which are arranged in an orderly fashion. However, if the B- and B'-
site cation are similar enough, they can form a randomly distributed perovskite, wherein 
no such ordering is present. The effect of the ordering of the B-/B'-site cations (rocksalt 
type & random) was investigated by synthesizing and investigating an iridium containing 
perovskite with randomly distributed B-/B'-octahedra. For this, part of the titanium cations 
in the cubic perovskite SrTiO$_3$ were replaced by iridium to yield SrTi$_{1.75}$Ir$_{0.25}$O$_3$ (hereafter 
denoted SrTiO$_3$:Ir(25%)).

Rietveld refinements using the X-ray powder diffraction data of SrTiO$_3$:Ir(25%) 
carried out for $Pm\bar{3}m$ yielded satisfactory results for the incorporation of iridium on the 
titanium sites. On convergence, the agreement factors read $R_{wp} = 5.86\%$, $R_{p} = 4.20\%$ and 
$\chi^2 = 1.80$, with a refined cell parameter of $a = 3.91413(9)$ Å. The observed and refined 
profiles are plotted in Figure 7.

The refined lattice parameter is slightly larger than the known lattice parameter 
for SrTiO$_3$ without iridium ($a = 3.845$ Å). This difference can be attributed to the fact that 
the ionic radius of iridium is larger than that of titanium, and thus incorporation of iridium 
in the lattice increases the cell constant.

It was also found that iridium is not easily incorporated in a randomly distributed 
perovskite-structure, with many attempts at forming a disordered perovskite (e.g. BaPb$_1$-$
_x$Ir$_x$O$_3$, BaZr$_{1-x}$Ir$_x$O$_3$, SrPb$_{1-x}$Ir$_x$O$_3$, and BaTi$_{1-x}$Ir$_x$O$_3$) being unsuccessful. Increasing the 
iridium content beyond 25% in SrTi$_{1-x}$Ir$_x$O$_3$ was also unsuccessful, with the formation of a 
contaminant Sr$_2$IrO$_4$-phase observed for higher iridium levels. As such, SrTiO$_3$:Ir(25%) is 
the only randomly distributed iridium containing perovskite reported in this work. The 
measured catalytic activity of SrTiO$_3$:Ir(25%) is plotted in Figure 8. Due to the evidently 
lower activity than double perovskites, only cyclic voltammetry was utilized to explore the 
catalytic behaviour. CVs of both commercial and nanosized IrO$_2$ are added as references.

As can be seen in Figure 8, SrTiO$_3$:Ir(25%) shows activity comparable to that of 
commercial IrO$_2$, but inferior to that of IrO$_2$ NPs. Although the number of iridium ions per 
mole is half of that in the double perovskites previously plotted, this appears not sufficient 
enough a change to be responsible this steep decrease in observed catalytic activity.

Effect of iridium site doping on catalytic activity: In an attempt to further decrease 
the iridium content in double perovskites, B'-site doping was attempted. Substitution of 
half of the iridium was attempted with both niobium and tantalum.

Rietveld refinement was carried out for these compounds in order to determine 
the degree of mixing that had occurred. For Ba$_2$Pr(Nb$_{0.5}$Ir$_{0.5}$)O$_6$, all peaks in the XRD 
pattern were observed to have a shoulder, indicative of an additional phase. Therefore, 
the Rietveld refinement was carried out for a mixture of two phases:
Phase 1: \( \text{Ba}_2\text{Pr}(\text{Ir}_{\alpha-x}\text{Nb}_x)\text{O}_6 \) (spacegroup \( Fm\overline{3}m \))

Phase 2: \( \text{Ba}_2\text{Pr}(\text{Nb}_{1-y}\text{Ir}_y)\text{O}_6 \) (spacegroup \( I\overline{2}m \))

\( \text{Ba}_2\text{PrIr}_x\text{O}_6 \) is known to form the first phase, while \( \text{Ba}_2\text{PrNb}_x\text{O}_6 \) is known to form the second phase. This refinement was found to satisfactorily describe the experimentally obtained XRD pattern on convergence. In the end, the agreement factors read: \( R_{wp} = 5.73\% \), \( R_b = 4.29\% \) and \( \chi^2 = 0.95 \). In Figure 9 the observed and calculated profiles of \( \text{Ba}_2\text{Pr}(\text{Nb}_{0.5}\text{Ir}_{0.5})\text{O}_6 \) are shown.

For Phase 1, a value of 0.5 was found for \( x \), whilst for Phase 2, \( y \) was determined to be 0.35. This indicates that a phase transition occurs from the lower symmetry \( I\overline{2}m \) phase to the higher symmetry \( Fm\overline{3}m \) phase with increasing iridium content. Even though doping with niobium did not result in a single phase product, the two main phases present both contain a mixture of \( B'-\)site cations (i.e. neither phase contains solely iridium or niobium on the \( B' \)-site).

For \( \text{Ba}_2\text{Pr}(\text{Ta}_{0.5}\text{Ir}_{0.5})\text{O}_6 \) a single phase was found to be sufficient to describe the obtained XRD pattern. Due to the observed peak splitting, the lower symmetry \( I\overline{2}m \) phase was used for the refinement, yielding satisfactory results. On convergence, the agreement factors read: \( R_{wp} = 7.03\% \), \( R_b = 4.96\% \) and \( \chi^2 = 1.52 \).

In Figure 10 the observed and calculated profiles of \( \text{Ba}_2\text{Pr}(\text{Ta}_{0.5}\text{Ir}_{0.5})\text{O}_6 \) are shown. Comparing \( \text{Ba}_2\text{Pr}(\text{Nb}_{0.5}\text{Ir}_{0.5})\text{O}_6 \) with \( \text{Ba}_2\text{Pr}(\text{Ta}_{0.5}\text{Ir}_{0.5})\text{O}_6 \), it looks that tantalum mixes more readily than niobium, with tantalum forming a single homogeneous mixed phase while niobium forms a mixture of phases, each with slightly different ratios of Nb and Ir. The catalytic activity of both these compounds was explored via cyclic voltammetry, and the obtained CVs are plotted in Figure 11, with commercial and nanosized \( \text{IrO}_2 \) added as references.

Both Ta and Nb doped double perovskites show a maximum at 1.675 V (see Figure 11, denoted *), with activity decreasing again at higher potentials. This peak is related to oxygen production, but a maximum is only seen during the first scan. After the first cycle, catalytic activity is observed to decrease drastically. This behaviour suggests that preferably, iridium is not partially substituted with other elements, as this may negatively affect the stability of double perovskites.

Similar to \( \text{SrTiO}_3:\text{Ir}(25\%) \), catalytic activity is comparable with commercial \( \text{IrO}_2 \), but inferior with respect to nanosized \( \text{IrO}_2 \). Again, the relative decrease in iridium content is not large enough to be responsible for the large observed decrease in catalytic activity. Even though \( B-/B' \)-site ordering is present in these compounds, a disorder of a different nature is introduced with the partial substitution of
iridium. Namely that iridium and the substitute cation are now randomly distributed on the B'-sites. Possibly, this statistical distribution of cations at the B'-sites is cause for the observed decrease in activity.

Effect of iridium replacement on catalytic activity: In order to determine whether iridium is the active site, a double perovskite where iridium was replaced with ruthenium (Ba₂PrIrO₆) was also tested for its catalytic properties and compared to the iridium containing variant (Ba₂PrIrO₆). Even though RuO₂ is slightly more active than IrO₂ in acidic media, the ruthenium containing double perovskite shows considerably lower catalytic activity for OER than the iridium containing double perovskite, as can be seen in Figure 12. The fact that surface normalized catalytic activity is so different makes it clear that iridium must be the active site.

Double perovskites in alkaline media: During the course of this work, it was observed that catalytic activity of Ba₂PrIrO₆ was different when measured in either 0.1 M NaOH or 0.1 M KOH. Therefore a series of 0.1M MOH solutions with different complementary cationic species (M = Li, Na, K, Rb, Cs) was prepared, and catalytic activity of Ba₂PrIrO₆ was determined in each of these media.

This resulted in the data shown in Figure 13. In Figure 14, the specific activity of Ba₂PrIrO₆ in 0.1 M RbOH is compared to the specific activity of Ba₂PrIrO₆ in 0.1 M HClO₄, with commercial and nanosized IrO₂ added as references. Catalytic activity of Ba₂PrIrO₆ in 0.1 M RbOH falls in between the activity of commercial and nanosized IrO₂. However the onset of oxygen evolution is delayed as compared to acidic media. The delay in onset, together with a higher Tafel slope, results in a somewhat reduced catalytic performance. It must be noted that iridium oxide is known to exhibit slightly higher catalytic performance in acidic media as compared to alkaline media, so this comparison is slightly biased.

However, catalytic performance of double perovskites in even the most active alkaline medium is lower as compared to the catalytic activity of the same compound in acidic media. This behaviour makes acidic media more interesting than alkaline media, when one is interested in high OER activity.

Further comparative examples: Related compounds in acidic media: Two iridium containing metal oxides with different structures were synthesized and investigated for their catalytic properties. Sr₂IrO₄ was selected because of the resemblance of the crystal structure to that of double perovskites. This compound belongs to the A₀₋₁A₂B₆O₃₋₄₋₁ (Ruddlesden-Popper) family, consisting of 2D alternating perovskite and rock-salt planes.

Meanwhile, Pr₂IrO₇ adopts a Fluorite-like structure, which bears little, if any, resemblance to the double perovskite structure. This structure contains octahedrally surrounded iridium ions, which are corner-linked to only two other octahedra each,
resulting in one-dimensional chains. This as opposed to Sr$_2$IrO$_4$, which contains two-dimensional layers of corner-linked iridium octahedra, and A$_2$BB’O$_6$ double perovskites, which consist of a three-dimensional space filled with corner-linked octahedra. Together, these compounds were utilized to probe the effect of the crystal structure on the catalytic activity of iridium containing double perovskites. The catalytic activity of both compounds is plotted in Figure 15, and compared to the catalytic activity of Ba$_2$PtIrO$_6$, commercial IrO$_2$ and IrO$_2$ NPs. Interestingly, Sr$_2$IrO$_4$ shows catalytic activity for OER comparable to that of double perovskites, suggesting that a two-dimensional perovskite layer is sufficient for the increased performance displayed by double perovskites. And while Pr$_3$IrO$_7$

exhibits activity which is comparable to the activity of nanosized IrO$_2$, it is considerably less active than double perovskites. However, ultimately both compounds are very unstable under electrochemical conditions in acid, which results in a steep drop in catalytic activity within seconds.

Summarising, applicants have shown convincingly the good electrochemical properties of A$_2$BIrO$_6$ double perovskites

In the subject electrocatalysts, the transition metal, Iridium, Ruthenium, Osmium, Rhenium, Rhodium, and/or combinations thereof, preferably Iridium or ruthenium, was found to be the active site for water oxidation with catalytic activity dependant on the pH of the electrolyte (lower pH higher activity), and the complementary cationic species (in alkaline media). B-site cation substitution showed only a minor effect on catalytic activity, and is therefore considered as not responsible for the remarkable jump in activity as compared to IrO$_2$.

The oxidation state of the metal, e.g. iridium, which is linked to the cation residing on the B-site, does not exhibit superior activity in either the 4+ or 5+ state. Changing the cation residing on the A-site was shown to allow to fine tune the catalytic activity.

However, as was the case for the cation residing on the B-site, the cation present at the A-site is not responsible for the jump in activity as compared to IrO$_2$. Albeit not responsible for the remarkable shift in catalytic activity, the cations present at the A- and B-site were found to have a prominent effect on catalyst stability and relative catalytic activity.
CONCLUSIES

1. Elektro-katalysator, geschikt voor de productie van zuurstof in elektrolytische processen, een perovskiet-achtige dubbele perovskiet-verbinding omvattende met de volgende algemene formule: $A_{n-1}(BB')_{n/2}O_{3n-1}$, waarbij B staat voor iridium, ruthenium, osmium, rhenium, rhodium, en/of combinaties van de voorgaande.

2. Elektro-katalysator volgens conclusie 1, waarbij elk B'-atoom is opgesteld in een octahedrale zuurstofcoördinatie.

3. Elektro-katalysator volgens conclusie 1 of conclusie 2, waarbij de verbinding ten minste gedeeltelijk in het bezit is van een gelaagde kristallijne perovskiet-structuur of van een dubbele kristallijne perovskiet-structuur.

4. Elektro-katalysator volgens een der conclusies 1 tot en met 3, waarbij B is geselecteerd uit de zeldzame aarden, zoals de lanthaniden of actiniden, of mengsels daarvan.

5. Elektro-katalysator volgens conclusie 4, waarbij B is geselecteerd uit La, Ce, Pr, Nd, Tb, en/of Y.

6. Elektro-katalysator volgens conclusie 4, waarbij B bij voorkeur aanwezig is in de 3⁺ of 4⁺ trap.

7. Elektro-katalysator volgens een der conclusies 4 tot en met 6, waarbij B is geselecteerd uit de groep die bestaat uit Ce, Nd, Pr, La, Lu, of combinaties daarvan.

8. Elektro-katalysator volgens een der voorgaande conclusies, waarbij A staat voor (AA')/2.

10. Elektro-katalysator volgens een der voorgaande conclusies, bovendien een metaalsubstraat omvattende.

11. Elektro-katalysator volgens conclusie 10, waarbij een laag van een perovskietachtig dubbel perovskiet elektro-katalytisch materiaal is voorzien op de buitenzijde van het metaalsubstraat.


13. Elektro-katalysator volgens een der conclusies 1 tot en met 11, waarbij het perovskiet-achtige dubbele perovskiet is geselecteerd uit de groep die bestaat uit $\text{Ba}_2\text{CeIrO}_6$, $\text{Ba}_2\text{NdIrO}_6$, $\text{Ba}_2\text{TbIrO}_6$ en $\text{Sr}_2\text{YIrO}_6$, $\text{Ba}_2\text{YIrO}_6$, $\text{Sr}_2\text{IrO}_4$, of welke combinatie daarvan dan ook.

14. Werkwijze voor de productie van een elektro-katalysatormateriaal volgens een der conclusies 1 tot en met 12, waarbij de werkwijze omvat:
   a) het voorzien van een mengsel van geschikte precursor-metaalzouten met een deeltjesgrootte en een vorm die geschikt zijn voor de bereiding;
   b) het blootstellen van het mengsel aan een temperatuur die gelegen is in het bereik van 850 °C tot 950 °C, en dit gedurende een geschikte periode, en
   c) het sinteren van het resulterende poeder bij een temperatuur die gelegen is in het bereik van 1200 °C tot 1300 °C, en die beter gelegen is in het bereik van 1225 °C tot 1275 °C, en dit gedurende een geschikte periode, optioneel gepaard gaand met het frequent tussentijds opnieuw malen, en
   d) het afkoelen van de verkregen monsters tot kamertemperatuur.

15. Werkwijze voor de productie van een elektro-katalysatormateriaal volgens een der conclusies 1 tot en met 12, waarbij de werkwijze omvat:
   i. het bereiden van een eerste oplossing die de precursor van de materialen omvat, en
   ii. het uit de oplossing afzetten van de materiaalprecursor op een metaalsubstraat door middel van een geïnduceerde wijziging van de
oplosbaarheid, bij voorkeur door middel van een kathodische elektroafzetting, en

iii. het onderwerpen van het aldus afgezette gevormde substraat aan een thermische behandeling bij een temperatuur die gelegen is in het bereik van 300 °C tot 1300 °C,

waarbij het materiaal gevormd wordt dat ten minste gedeeltelijk in het bezit is van een dubbele perovskiet-structuur.

16. Gebruik van een perovskiet-achtige dubbele perovskiet AA′BB′O6 volgens een der conclusies 1 tot en met 13, of de samenstelling die kan verkregen worden aan de hand van de werkwijze volgens een der conclusies 14 of 15, als katalysator.

17. Werkwijze voor het splitsen van water in zuurstof en protonen door middel van electrolyse, waarbij een samenstelling volgens een der conclusies 1 tot en met 13 wordt gebruikt in een elektrode.

18. Werkwijze volgens conclusie 17, waarbij de pH van het procesmedium gelegen is in het bereik van 0 tot 5,5.

19. Werkwijze volgens conclusie 17 of conclusie 18, waarbij de vereiste elektriciteit voor het electrolytische proces wordt geleverd door gebruik te maken van een duurzame bron van elektrische energie, geselecteerd uit windenergie, zonne-energie, golfenergie of getijde-energie.
Fig. 3
Abstract:

The present invention relates to an electrocatalyst suitable for oxygen evolution in electrolytic processes, such as the electrolysis of water, comprising a perovskite-like double perovskite compound having the following general formula: $A_{n+1} (BB')_{n/2} O_{3n+1}$, wherein B represents Iridium, Ruthenium, Osmium, Rhenium, Rhodium, and/or combinations thereof, and to methods of its preparation and use.
RAPPORT BETREFFENDE HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK

Octrooiaanvragen 2014577

<table>
<thead>
<tr>
<th>Classificatie van het onderwerp¹:</th>
</tr>
</thead>
<tbody>
<tr>
<td>B01123/46, B01123/36, C25B1/04</td>
</tr>
<tr>
<td>Onderzochte gebieden van de techniek¹:</td>
</tr>
<tr>
<td>B011, C25B</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Computerbestanden:</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPODOC, WPI</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Omvang van het onderzoek:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niet volledig wegens niet-eenheid van uitvinding</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Datum van de onderzochte conclusies:</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 juni 2015</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Niet onderzochte conclusies:</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
</tr>
</tbody>
</table>

Van belang zijnde literatuur

<table>
<thead>
<tr>
<th>Categorie²</th>
<th>Vermelding van literatuur met aanduiding, voor zover nodig, van speciaal van belang zijnde tekstgedeelten of figuren.</th>
<th>Van belang voor conclusie(s) nr.:</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 2013/0330651 A (THOMPSETT DAVID) 12 december 2013 * par. [0022], [0038], [0039] *</td>
<td>1-14, 16-19</td>
</tr>
</tbody>
</table>

Datum waarop het onderzoek werd voltooid: 8 september 2015

De bevoegde ambtenaar: Dr. M.W. de Lange

Octrooicentrum Nederland, onderdeel van Rijksdienst voor Ondernemend Nederland

¹ Gedetineerd volgens International Patent Classification (IPC).
² Verklaring van de categorie-aanduiding: zie apart blad.
Categorie van de vermelde literatuur:

X: op zichzelf van bijzonder belang zijnde stand van de techniek
Y: in samenhang met andere geciteerde literatuur van bijzonder belang zijnde stand van de techniek
A: niet tot de categorie X of Y behorende van belang zijnde stand van de techniek
O: verwijzend naar niet op schrift gestelde stand van de techniek
P: literatuur gepubliceerd tussen voorrangs- en indieningsdatum
T: niet tijdig gepubliceerde literatuur over theorie of principe ten grondslag liggend aan de uitvinding
E: octrooiliteratuur gepubliceerd op of na de indieningsdatum van de onderhavige aanvraage en waarvan de indieningsdatum of de voorrangsdatum ligt voor de indieningsdatum van de onderhavige aanvraage.
D: in de aanvraage genoemd
L: om andere redenen vermelde literatuur
&: lid van dezelfde octrooifamilie; corresponderende literatuur
**SCHRIJFTELIJKE OPINIE**

**Octrooiaanvraage 2014577**

<table>
<thead>
<tr>
<th>Indieningsdatum:</th>
<th>Voorangsdatum:</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 april 2015</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Classificatie van het onderwerp¹:</th>
<th>Aanvrager:</th>
</tr>
</thead>
<tbody>
<tr>
<td>B01J23/46, B01J23/36, C25B1/04</td>
<td>Universiteit Leiden</td>
</tr>
</tbody>
</table>

Deze schriftelijke opinie bevat een toelichting op de volgende onderdelen:

- ✔ Onderdeel I  Basis van de schriftelijke opinie
- □ Onderdeel II  Voorrang
- ✔ Onderdeel III  Vaststelling nieuwheid, inventiviteit en industriële toepasbaarheid niet mogelijk
- ✔ Onderdeel IV  De aanvraag heeft betrekking op meer dan één uitvinding
- ✔ Onderdeel V  Gemotiveerde verklaring ten aanzien van nieuwheid, inventiviteit en industriële toepasbaarheid
- □ Onderdeel VI  Andere geciteerde documenten
- □ Onderdeel VII  Overige gebreken
- □ Onderdeel VIII  Overige opmerkingen

---

De bevoegde ambtenaar:
Dr. M.W. de Lange

**Octrooicentrum Nederland,**
onderdeel van Rijksdienst voor Ondernemend Nederland

---

¹ Gedefinieerd volgens International Patent Classification (IPC).
Onderdeel I  Basis van de schriftelijke opinie

Deze schriftelijke opinie is opgesteld op basis van de op 15 juni 2015 ingediende conclusies.

Onderdeel III  Vaststelling nieuwheid, inventiviteit en industriële toepasbaarheid niet mogelijk

De vraag of de uitvinding in de aanvraag nieuw, inventief en industrieel toepasbaar is, wordt niet behandeld in deze schriftelijke opinie met betrekking tot:

dele gehele aanvraag
☒ conclusies 15

omdat:
☐ deze aanvraag of deze conclusies betrekking hebben op materie die geen uitvinding betreft op enig gebied van de technologie en daarom niet vatbaar is voor octrooi.
☐ deze aanvraag of deze conclusies betrekking hebben op materie die niet vatbaar is voor octrooi ingevolge artikel 3 van de Rijksoctroowlaw 1995.
☐ de beschrijving, figuren of deze conclusies, zo onduidelijk zijn dat het niet zinvol is een schriftelijke opinie op te stellen.
☐ deze conclusie onvoldoende steun vinden in de beschrijving waardoor het niet zinvol is een schriftelijke opinie op te stellen.
☒ geen onderzoek naar de stand van de techniek is uitgevoerd voor deze conclusies.
☐ een zinvolle schriftelijke opinie niet opgesteld kon worden omdat de sequentie opsomming niet beschikbaar was in het juiste formaat, of in het geheel niet beschikbaar was (WIPO ST25).
☐ een zinvolle schriftelijke opinie niet opgesteld kon worden zonder de tabellen met betrekking tot de sequentie opsommingen; of deze tabellen waren niet beschikbaar in elektronische vorm.

Toelichting:
Zie Onderdeel IV

Onderdeel IV  De aanvraag heeft betrekking op meer dan één uitvinding

Vastgesteld is dat de octrooiaanvraag betrekking heeft op meer dan één uitvinding. Het onderzoek naar de stand van de techniek is beperkt tot de eerstgenoemde uitvinding in de conclusies en betreft:

dele conclusies
☒ conclusies 1-14, 16-19

Toelichting:
Conclusies 14 en 15 beschrijven afzonderlijke werkwijzen voor de produktie van een elektro-katalysatormateriaal volgens conclusies 1-12. Aangezien het materiaal niet nieuw is (zie onderdeel V) berusten de werkwijzen niet op een gemeenschappelijke uitvindingsgedachte.
Onderdeel V  Gemotiveerde verklaring ten aanzien van nieuwdheid, inventiviteit en industriële toepasbaarheid

1. Verklaring

<table>
<thead>
<tr>
<th>Nieuwdheid</th>
<th>Ja : Conclusie(s) 14, 18, 19</th>
<th>Nee : Conclusie(s) 1-13, 16, 17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inventiviteit</td>
<td>Ja : Conclusie(s)</td>
<td>Nee : Conclusie(s) 14, 18, 19</td>
</tr>
<tr>
<td>Industriële toepasbaarheid</td>
<td>Ja : Conclusie(s) 1-14, 16-19</td>
<td>Nee : Conclusie(s)</td>
</tr>
</tbody>
</table>

2. Literatuur en toelichting

D1 = US 2013/0330651 A (THOMPSETT DAVID) 12 december 2013


Uit D1 is bekend een elektro-katalysator een perovskietachtige dubbele perovskiet-verbinding omvattende met de volgende algemene formule: SrM$_{0.5}$Ir$_{0.5}$O$_3$ waarbij M staat voor calcium, magnesium, of geselecteerd is uit de zeldzame aarden, zoals yttrium, lanthanum, cerium, praseodymium, neodymium, terbium, of lutetium. Voorts is uit D1 bekend het gebruik van deze katalysator in een celreactor voor het splitsen van water in zuurstof en protonen. Zie par. [0022], [0038], [0039].

Conclusies 1-13, 16-17 zijn niet nieuw in het licht van D1.

In de beschrijving van de onderhavige aanvraag worden als voorbeelden van de uitvinding een aantal dubbele perovskieten opgevoerd die bekend zijn uit D2, D3 of D4 en bereid zijn volgens de werkwijzen bekend uit D2, D3 en D4. Zoals blijkt uit de resultaten zijn deze verbindingen geschikt als katalysator voor de productie van zuurstof in elektrolytische processen. Conclusies 1-13 zijn niet nieuw in het licht van D2, D3 en D4.

D5 betreft een aankondiging van een lezing aan de katalyse vakgroep van de Universiteit Leiden. Uit de titel zal de gemiddelde vakman opmaken dat een dubbele perovskiet met iridium kan worden toegepast als katalysator in een celreactor voor het splitsen van water in zuurstof en protonen. Tenminste conclusies 1, 16 en 17 zijn niet nieuw in het licht van D5.

Uit elk van de documenten D2 en D3 is bekend een werkwijze voor de productie van een dubbele perovskiet volgens conclusie 1, waarbij de werkwijze omvat:

a) het voorzien van een mengsel van geschikte metaalprecursors, waaronder metaalzouten, met een deeltjesgrootte en een vorm die geschikt zijn voor de bereiding;
Schriftelijke Opinie

Octrooiaanvraag 2014577

b) het blootstellen van het mengsel aan een temperatuur die gelegen is in het bereik van 850°C tot 950°C, en dit gedurende een geschikte periode, en
c) het sinteren van het resulterende poeder bij een temperatuur die gelegen is in het bereik van 1200°C tot 1300°C, en dit gedurende een geschikte periode, optioneel gepaard gaand met het frequent tussentijds opnieuw malen, en
d) het afkoelen van de verkregen monsters tot kamertemperatuur.

Zie par.2 Experimental.

Ten opzichte van dit bekende blijft als onderscheidend kenmerk van conclusie 14 over dat alle metaalprecursors metaalzouten zijn. Metaalzouten zijn gebruikelijke uitgangsstoffen voor de vorming van perovskieten. Conclusie 14 is daarom niet inventief in het licht van D2 en D3.

De resterende volgconclusies 18 en 19 zijn gericht op maatregelen die worden beschouwd als niet meer dan een van verschillende mogelijkheden die de vakman afhankelijk van de omstandigheden zal selecteren zonder het uitoefenen van inventieve vaardigheid.