

RUTHENIUM-BASED ELECTROCATALYST FOR OXYGEN EVOLUTION IN ACIDIC MEDIA

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority to the Singapore application no. 10202250487W filed 15 July 2022, the contents of which is hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] This application relates to a ruthenium-based electrocatalyst. In particular, the application relates to a ruthenium-based electrocatalyst for oxygen evolution in acidic media and a method for preparing the ruthenium-based electrocatalyst.

BACKGROUND

[0003] Hydrogen fuel is regarded as a promising energy carrier to replace conventional fossil fuels for a sustainable energy future. A clean and sustainable hydrogen economy can be truly established only when hydrogen is made from water splitting technology driven by renewable energy sources such as wind and solar. Proton-exchange membrane (PEM) electrolysis for hydrogen production has demonstrated many exclusive advantages over alkaline water electrolysis, including higher current density, higher purity of pressurized hydrogen, more compact and portable electrolyzer system, and importantly, much better compatibility with intermittent/discontinuous renewable energy sources. Nevertheless, large-scale implementation of PEM electrolyzer has been restricted by its precious catalysts, particularly the lack of durable, efficient, and cost-effective electrocatalyst for oxygen evolution reaction (OER) in harsh acidic media. To date, precious ruthenium/iridium-based

compounds are the commercial electrocatalyst for acidic oxygen evolution reaction. Compared with iridium oxide, ruthenium oxide (RuO_2) possesses higher oxygen evolution reaction activity and lower cost, but also poorer stability as compared to iridium oxide.

[0004] Tremendous efforts have been dedicated to exploring ways to improve both stability and activity of ruthenium-based oxygen evolution reaction catalysts as the reported ruthenium-based catalysts are still far from practical applications in terms of stability. Many approaches focus on structural modification of the crystal or crystalline phase, as well as doping or compounding based on the ruthenium oxide itself, which inevitably introduce ruthenium oxides (RuO_2) crystal in the catalyst, leading to oxidative degradation at low anodic potential under acidic conditions.

[0005] It is therefore desirable to provide a ruthenium-based electrocatalyst and a method that seek to address at least one of the problems described hereinabove, or at least to provide an alternative.

SUMMARY

[0006] According to a first aspect of the present disclosure, a ruthenium-based electrocatalyst is provided. The ruthenium-based electrocatalyst comprises ruthenium oxychloride species having a general formula RuOCl_y , dispersed in a manganese oxide support having a general formula MnO_x .

[0007] In some embodiments, the ruthenium-based electrocatalyst further comprises a substrate, wherein the ruthenium-based electrocatalyst is disposed onto at least one surface of the substrate.

[0008] According to a second aspect of the present disclosure, a method of preparing a ruthenium-based electrocatalyst is provided. The method comprises heating a substrate; adding a precursor solution containing a chloride salt of ruthenium and a nitrate salt of manganese onto the substrate; and heating the precursor solution with the substrate to obtain a ruthenium-

based electrocatalyst comprising ruthenium oxychloride species having a general formula RuOCl_y , dispersed in a manganese oxide support having a general formula MnO_x .

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Various embodiments of the present disclosure are described hereinbelow in the detailed description with reference to the following drawings:

FIG. 1 is a flowchart of an example method of fabricating a ruthenium-based electrocatalyst in accordance with certain embodiments described herein.

FIG. 2 is a schematic diagram of oxygen evolution reaction (OER) on the electrocatalyst by dispersing active ruthenium oxychloride (RuOCl_y) species in a manganese oxide (MnO_x) support in accordance with an embodiment of the present disclosure.

FIG. 3 illustrates XRD spectra of (A) RuOCl@MnO_x , (B) MnO_x , (C) RuOCl , (D) glass, and (E) pure RuO_2 samples.

FIG. 4 illustrates Raman spectra of (A) RuOCl@MnO_x , (B) MnO_x , and (C) RuOCl samples.

FIG. 5 illustrates XPS full spectra of (A) RuOCl@MnO_x , (B) RuOCl , and (C) MnO_x .

FIG. 6 illustrates XPS spectra of Ru 3p of (A) RuOCl@MnO_x , and (B) RuOCl .

FIG. 7 illustrates XPS spectra of Ru 3d/C 1s of RuOCl@MnO_x . Sat. represents the satellite peaks of Ru 3d.

FIG. 8 illustrates XPS spectra of Cl 2p of (A) RuOCl@MnO_x , and (B) RuOCl .

FIG. 9 illustrates XPS spectra of O 1s of (A) RuOCl@MnO_x , and (B) MnO_x .

FIG. 10 illustrates XPS spectra of Mn 2p states of (A) RuOCl@MnO_x , and (B) MnO_x .

FIG. 11 shows the atomic ratios obtained from the XPS results, where the atomic concentrations are normalized to that of Ru in the RuOCl@MnO_x and RuOCl samples, and to that of Mn in MnO_x sample.

FIG. 12(a) shows the Ru K-edge normalized XANES (X-ray absorption near edge spectroscopy) spectra and FIG. 12(b) shows the derivative normalized XANES spectra of (A)

RuOCl@MnO_x on carbon fiber paper, (B) RuOCl@MnO_x powder, (C) RuO₂ standard, (D) RuCl₃ standard, and (E) ruthenium foil. FIG. 12(c) shows the Mn K-edge normalized XANES spectra and FIG. 12(d) shows the derivative normalized XANES spectra of (A) RuOCl@MnO_x on carbon fiber paper, (B) RuOCl@MnO_x powder, (C) MnO₂ standard, (D) manganese (III) oxide (Mn₂O₃) standard, (E) MnCl₂·xH₂O standard, and (F) manganese foil. FIG. 12(e) and (f) show the standard-driven linear regression for Ru and Mn samples, respectively.

FIG. 13(a) is a HRTEM image of RuOCl@MnO_x. FIG. 13(b) shows a SAED (selected area electron diffraction) pattern of RuOCl@MnO_x, which shows faint diffraction rings corresponding to (222), (411), (521) and (622) planes of Mn₂O₃.

FIG. 13(c) shows an AC HAADF-STEM image of RuOCl@MnO_x. FIG. 13(d) shows a HAADF-STEM image and the corresponding STEM-EDS mapping of (e) Ru, (f) Cl, (g) O, and (h) Mn, respectively.

FIG. 13(i) shows the Ru K-edge FT-EXAFS (extended x-ray absorption fine structure) spectra of (A) RuOCl@MnO_x, (B) RuO₂ standard, (C) RuCl₃ standard, and (D) ruthenium foil. FIG. 13(j) shows the Mn K-edge FT-EXAFS spectra of (A) RuOCl@MnO_x powder, (B) RuOCl@MnO_x on carbon fiber paper (CFP), (C) MnCl₂ standard, and (D) manganese foil.

FIG. 13(k) shows the energy dispersion spectrum of RuOCl@MnO_x. FIG. 13(l) shows the atomic ratios obtained from EDS (energy dispersive spectrometer) results, where the atomic concentrations are normalized to that of Ru in (A) RuOCl@MnO_x, and (B) RuOCl samples, and to that of Mn in (C) MnO_x.

FIG. 14 shows TEM images of (a) RuOCl@MnO_x, and (b) RuOCl, and EELS (electron energy loss spectroscopy) patterns of (c) RuOCl@MnO_x, and (d) RuOCl samples.

FIG. 15 shows SEM images of (a) RuOCl@MnO_x, (b) MnO_x, and (c) RuOCl.

FIG. 16(a) shows the SEM-EDS image of the RuOCl@MnO_x sample, and the Ru L α , Cl K α , O K α , and Mn K α SEM-EDS mappings.

FIG. 16(b) shows the SEM-EDS image of the RuOCl sample and the Ru L α , Cl K α , O K α , C K α SEM-EDS mappings.

FIG. 17(a) is a graph showing the chronopotentiometry curves of (A) RuOCl@MnO_x, (B) RuOCl, (C) MnO_x, (D) RuO₂|1.05@CFP, (E) RuO₂|0.15@CFP, (F) RuOCl/MnO_x, (G) RuO₂/MnO_x, and (H) carbon fiber paper (CFP) at a current density of 10 mA cm⁻². The inset is enlarged curves within 25 h. FIG. 17(b) is a graph showing the chronopotentiometry curves of RuOCl@MnO_x at current densities of 100 mA cm⁻², 300 mA cm⁻², and 500 mA cm⁻² without iR correction. FIG. 17(c) is a graph showing the polarization curves of (A) RuOCl@MnO_x, (B) MnO_x, (C) RuO₂|0.15@CFP, and (D) RuO₂|1.05@CFP.

FIG. 18 is a graph showing the overpotentials at 10 mA cm⁻² (η_{10}) of RuOCl@MnO_x, RuO₂|1.05@CFP, RuO₂|0.15@CFP, and MnO_x, and mass activity of RuOCl@MnO_x, RuO₂|1.05@CFP, and RuO₂|0.15@CFP at an overpotential of 300 mV.

FIG. 19 is a graph showing the LSV curves of RuOCl for the (1) first, (2) second and (3) third tests, and the LSV curve of (A) RuOCl@MnO_x.

FIG. 20(a) is a graph showing the LSV curves of RuO₂|x@CFP (x= (i) 0.15, (ii) 0.3, (iii) 0.45, (iv) 0.6, (v) 0.75, (vi) 0.9, (vii) 1.05). FIG. 20(b) is a TEM image of a commercially purchased RuO₂.

FIG. 21 is a graph showing the mass activity of (A) RuOCl@MnO_x, (B) RuO₂|0.15@CFP, and (C) RuO₂|1.05@CFP.

FIG. 22 shows Tafel plots of (A) RuOCl@MnO_x (43 mV dec⁻¹), (B) RuO₂|1.05@CFP (48 mV dec⁻¹) and (C) RuO₂|0.15@CFP (53 mV dec⁻¹).

FIG. 23 shows SEM images of RuOCl@MnO_x before (a-c) and after (d-f) 280-h stability test with enlarged magnification from left to right.

FIG. 24 illustrates XRD spectra of initial RuOCl@MnO_x, and that after 280-h stability test, and carbon fiber paper (CFP).

FIG. 25 is a HRTEM image of RuOCl@MnO_x, after 280-h stability test at 10 mA cm⁻².

FIG. 26(a) illustrates Raman spectra of RuOCl@MnO_x (A) before and (B) after 280-h stability test. FIG. 26(b) illustrates XPS spectra of Ru 3p state of (A) initial RuOCl@MnO_x, and that (B) after 48-h stability test, and (C) after 280-h stability test. FIG. 26(c) shows the normalized Ru K-edge XANES spectra of (A) initial RuOCl@MnO_x, (B) RuOCl@MnO_x after 48-h stability test, (C) ruthenium foil, (D) RuCl₃ standard, and (E) RuO₂ standard. FIG. 26(d) shows the normalized Mn K-edge XANES spectra of (A) initial RuOCl@MnO_x, (B) RuOCl@MnO_x after 48-h stability test, (C) MnCl₂·xH₂O standard, (D) Mn₂O₃ standard, and (E) MnO₂ standard. FIGs. 26(e) and (f) illustrate XPS spectra of Mn 2p and Cl 2p states, respectively of (A) initial RuOCl@MnO_x, and that (B) after 48-h stability test, and (C) after 280-h stability test.

FIGs. 27(a) and (b) illustrate XPS spectra of O 1s and C 1s/Ru 3d states, respectively of (A) initial RuOCl@MnO_x, and that (B) after 48-h stability test, and (C) after 280-h stability test at 10 mA cm⁻². The C 1s peaks have been corrected to 284.8 eV.

FIG. 28 shows SEM images and SEM-EDS full element mappings (scale bar: 1 μm) of RuOCl@MnO_x after (a-c) 200-h stability test at 100 mA cm⁻², (d-f) 100-h stability test at 300 mA cm⁻², and (g-i) 50-h stability test at 500 mA cm⁻².

FIG. 29 shows HRTEM images of RuOCl@MnO_x after (a) 200-h stability test at 100 mA cm⁻², (b) 100-h stability test at 300 mA cm⁻², and (c) 50-h stability test at 500 mA cm⁻².

FIG. 30 illustrates Raman spectra of (A) initial RuOCl@MnO_x, and that (B) after 200-h stability test at 100 mA cm⁻², (C) after 100-h stability test at 300 mA cm⁻², and (D) after 50-h stability test at 500 mA cm⁻².

FIG. 31 illustrates XPS spectra of (a) Ru 3p, (b) Mn 2p, and (c) O 1s states of (A) initial RuOCl@MnO_x, and that (B) after 200-h stability test at 100 mA cm⁻², (C) after 100-h stability test at 300 mA cm⁻², and (D) after 50-h stability test at 500 mA cm⁻².

FIG. 32 is a Pourbaix diagram of 89-11% Mn-Ru system in aqueous solution based on a reported method (Toma, F. M., et al., "Mechanistic insights into chemical and photochemical transformations of bismuth vanadate photoanodes", *Nat. Commun.* 7, 12012 (2016)), assuming Mn and Ru ion concentration at 10⁻⁸ mol.kg⁻¹. RuO₄(aq) is appropriate here to describe the state of Ru at high positive potentials. Regions are labelled for stable phases of: A-MnO₄+RuO₄(aq); B-Mn³⁺+RuO₄(aq); C-Mn²⁺+RuO₄(aq); D-MnO₂(s)+RuO₄(aq); E-Mn²⁺+Ru(OH)₂²⁺; F-Mn²⁺+RuO₂(s); G-Mn₂O₃(s)+RuO₄(aq); H-MnO₄²⁻+RuO₄(aq); I-Mn₂O₃(s)+RuO₂(s); J-Mn²⁺+Ru(s); K-Mn₃O₄(s)+RuO₂(s); L-MnOH⁺+RuO₂(s); M-Mn(OH)₃-+RuO₂(s); N-MnOH⁺+Ru(s); O-Mn(OH)₃-+Ru(s); P-Mn²⁺+MnRu₃(s); Q-MnOH⁺+MnRu₃(s); R-Mn(OH)₃-+MnRu₃(s); S-Mn(s)+MnRu₃(s).

FIG. 33(a) is a graph showing slow scan linear scanning voltammetry (LSV) curves extended to high anodic potential without iR correction. FIG. 33(b) is a plot showing the formation energies of bulk and (010) surface energies for RuO₂, Mn₂O₃, and Mn₂O₃Ru. FIG. 33(c) is a graph showing the free-energy profiles of oxygen evolution reaction on different surfaces such as (A) Ru2 site on Mn₂O₃Ru (110), (B) RuO₂, (C) Ru1 site on Mn₂O₃Ru (110) surface, and (D) Mn site on Mn₂O₃Ru (110), whereby the theoretical overpotentials are 0.75, 0.99, 1.11 and 1.32V, respectively. (E) is the ideal catalyst. The unit of Gibbs free energy is eV. FIG. 33(d) illustrates the geometric structures and intermediates for oxygen evolution reaction on different surfaces, where Ru, Mn, O, and H atoms are shown.

FIG. 34 shows established simulation models in bulk forms and calculated bond lengths after structural optimization of RuO₂, Mn₂O₃, and Mn₂O₃Ru, where Ru, O, and Mn atoms are shown.

FIG. 35 shows a comparison of structure units on the (110) surface without vacancy defects (upper) and with vacancy defects (lower) of RuO₂, Ru1 in Mn₂O₃Ru, and Ru2 in Mn₂O₃Ru.

DETAILED DESCRIPTION

[0010] The following detailed description is made with reference to the accompanying drawings, showing details and embodiments of the present disclosure for the purposes of illustration. Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments, even if not explicitly described in these other embodiments. Additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0011] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0012] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance as generally understood in the relevant technical field, e.g., within 10% of the specified value.

[0013] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0014] As used herein, “comprising” means including, but not limited to, whatever follows the word “comprising”. Thus, use of the term “comprising” indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[0015] As used herein, “consisting of” means including, and limited to, whatever follows the phrase “consisting of”. Thus, use of the phrase “consisting of” indicates that the listed elements are required or mandatory, and that no other elements may be present.

[0016] A detailed description of various embodiments will be described below with reference to the drawings.

[0017] The present disclosure relates to an electrocatalyst. It belongs to the fields involving electrochemistry, materials synthesis, catalysis, water electrolysis, hydrogen energy, battery, etc. In particular, it relates to a ruthenium-based electrocatalyst. The ruthenium-based electrocatalyst comprises ruthenium oxychloride species having a general formula RuOCl_y , dispersed in a manganese oxide support having a general formula MnO_x . In various embodiments, y represents a number of 0.2 to 1.6, and x represents a number 1.7 to 1.8.

[0018] In various embodiments, the ruthenium-based electrocatalyst is referred to as RuOCl@MnO_x . The term " RuOCl@MnO_x " as used herein refers to a ruthenium-based electrocatalyst comprising ruthenium oxychloride (RuOCl_y) species dispersed in a manganese oxide (MnO_x) support wherein chemical bondings between the ruthenium oxychloride (RuOCl_y) species and the manganese oxide (MnO_x) support are formed.

[0019] In various embodiments, the molar ratio of RuOCl_y to MnO_x is 1:11.1 or 1:7.8.

[0020] In various embodiments, the Ru:Cl:O ratio in RuOCl is 1:0.4:2.4 or 1:0.2:2.1.

[0021] In various embodiments, the Mn:O ratio in MnO_x is 1:1.7 or 1:1.8.

[0022] In various embodiments, the Ru:Cl:O:Mn ratio in RuOCl@MnO_x is 1:1.6:18.0:11.1.

[0023] In one embodiment, the electrocatalyst is composed of amorphous nanoparticles with tiny nanocrystals.

[0024] In one embodiment, the ruthenium-based electrocatalyst may further include carbon black powder dispersed in the manganese oxide (MnO_x) support.

[0025] In various embodiments, the ruthenium-based electrocatalyst further comprises a substrate, wherein the ruthenium oxychloride species and the manganese oxide support are dispersed within the substrate. In various embodiments, the substrate is porous, mesoporous

or microporous. Examples of suitable substrate materials include, but are not limited to, any carbon-based porous material including carbon cloth, carbon cloth covered by a thinner microporous layer consisting of carbon black powder, carbon fiber paper consisting of carbon black powder, macroporous carbon fiber paper, carbon nanotube film, graphene film, and other carbon-based materials that have mesoporous structure and good electrical conductivity.

In one embodiment, the substrate is a carbon fiber paper.

[0026] The structure of the electrocatalyst of the present disclosure helps to break the bonding structure of Ru-O-Ru in the ruthenium oxide (RuO_2) crystal structure with the help of the manganese oxide (MnO_x) support to improve the stability performance of ruthenium-based catalytic materials. The stability is further enhanced with the help of Ru-O-Mn bonding which is formed when the ruthenium oxychloride species (RuOCl_y) are dispersed in the MnO_x support. The electrocatalyst is constructed via a rational catalytic system design and the selection of suitable support material, material preparation and structure optimization on the catalytic performance and the catalytic mechanism of acidic oxygen evolution reaction, particularly focusing on the intrinsic correlation between the support types, material system energy, interfacial binding, and catalytic stability enhancement.

[0027] The structure of the electrocatalyst also helps to improve the oxidant potential of ruthenium catalyst system by uniformly dispersing ruthenium in the bulk of the MnO_x support, thus avoiding formation of ruthenium oxide (RuO_2) crystals.

[0028] The halogen element of the ruthenium-based electrocatalyst helps to increase the stability of the eletrocatalyst. In one embodiment, the halogen element is chlorine (Cl). In other embodiments, the halogen element can be florine (Fl) or bromine (Br).

[0029] In the present disclosure, a method of producing the ruthenium-based electrocatalyst is also provided. When deriving the method of the present disclosure, methods such as low-temperature one-step annealing method, multi-step annealing method and rapid

high-temperature sintering method have been explored. The method is derived by adjusting the parameters of temperature process, metal ratio of the ruthenium-based electrocatalyst, ligand structure of the ruthenium-based electrocatalyst, crystallization difference, and crystallinity of the ruthenium-based electrocatalyst. The method allows ruthenium mass loading to be minimized without apparently affecting its activity.

[0030] Referring to FIG. 1, the method comprises heating a substrate and adding a precursor solution containing a chloride salt of ruthenium and a nitrate salt of manganese onto the substrate. This is followed by heating the precursor solution with the substrate at a temperature for a predetermined duration to obtain a ruthenium-based electrocatalyst comprising ruthenium oxychloride species having a general formula RuOCl_y dispersed in a manganese oxide support having a general formula MnO_x . In various embodiments, y represents a number of 0.2 to 1.6, and x represents a number 1.7 to 1.8.

[0031] In various embodiments, the chloride salt of ruthenium is ruthenium (III) chloride (RuCl_3), and the nitrate salt of manganese is manganese (II) nitrate ($\text{Mn}(\text{NO}_3)_2$).

[0032] The Ru atoms from the ruthenium oxychloride (RuOCl_y) species bond to the O atoms from the manganese oxide (MnO_x) support to form dominant Ru-O-Mn and the residue Cl element is doped or chemisorbed onto the electrocatalyst body or micropores after oxidation of RuCl_3 precursor. The doped/chemisorbed Cl promotes the dispersion of Ru atoms and thus provides abundant active structural defects. The defect structure is introduced to the solid MnO_x support arising from the Ru atoms, and the doped/chemisorbed Cl atom further increases the unsaturated coordination defects. The active Ru atoms are encapsulated by the abundant Mn and O atoms, resulting in protective effect on the catalytic sites. Such a geometry of the electrocatalyst has several advantages including having similar octahedral coordination in ruthenium oxide (RuO_2) and manganese oxide (MnO_2) in their crystalline phase which renders $\text{RuOCl}@\text{MnO}_x$ material having compatible unit structure, thus

suppressing the trend of phase segregation. Another advantage is the amorphous characteristics of the electrocatalyst arising from the low synthesis temperature that increases the density of defect sites such as grain boundaries and edges, thereby increasing the catalytic activity. Another advantage is the use of MnO_x as the support. MnO_x material has excellent resistance to acid corrosion and oxidation, and this offers a reliable and stable support for the ruthenium-based electrocatalyst, thus breaking the aggregation of ruthenium oxide (RuO_2) and improving the oxidation potential. The electrocatalyst has excellent stability for acidic oxygen evolution reaction which is significantly enhanced by the dispersion of ruthenium in the stable MnO_x support. The MnO_x support has high resistance to acid and oxidation, and this helps to stabilize the encapsulated Ru species by inhibiting the formation of ruthenium oxide (RuO_2).

[0033] The Ru active sites significantly decrease the oxygen evolution reaction overpotential, and in turn slow down the decay of MnO_x support caused by its oxidation to MnO_4^- at high potential. The uniform dispersion of active Ru sites into the MnO_x support or matrix results in sustained oxygen evolution reaction operation with high activity at low Ru mass loading. This helps to reduce the cost of fabrication of the electrocatalyst and the product cost. Furthermore, both oxygen evolution reaction active RuO_2 and MnO_x with strong catalyst-support interaction work synergistically to enhance overall catalytic performances. The resulting electrocatalyst shows low overpotential of 228 mV at 10 mA cm^{-2} , great stability for 280 h at 10 mA cm^{-2} and 200 h at 100 A cm^{-2} in strong acidic media (0.5 M sulfuric acid, pH of 0.26), and low ruthenium loading of $0.105 \text{ mg}_{\text{Ru}}/\text{cm}^{-2}$, outperforming most reported ruthenium-based oxygen evolution reaction electrocatalysts. The electrocatalyst can be employed for use in PEM electrolyzer. The ruthenium-based electrocatalyst is capable of achieving higher energy conversion efficiency as compared to existing Ru/Ir-based catalysts in PEM electrolyzer. When the electrocatalyst is used in a PEM electrolyzer, the

electrocatalyst has a higher current density for water electrolysis as compared to existing Ru/Ir-based catalyst.

[0034] In various embodiments, the substrate and the precursor solution are heated to a temperature ranging from 200°C to 220°C, preferably 205°C to 215°C, more preferably 210°C. In various embodiments, the substrate and the precursor solution are heated for a duration sufficient for the bonds between the ruthenium oxychloride (RuOCl_y) species and the manganese oxide (MnO_x) support to form and to avoid the formation of highly crystalline phase and thus retaining a large number of defects. In various embodiments, the substrate and the precursor solution are heated for a duration between 8 and 20 min, preferably between 8 to 12 min, more preferably between 8 to 10 min.

[0035] In various embodiments, the substrate is porous, mesoporous or microporous, and the ruthenium oxychloride species and the manganese oxide support are dispersed within the substrate. Examples of suitable substrate materials include, but are not limited to, any carbon-based porous material including carbon cloth, carbon cloth covered by a thinner microporous layer consisting of carbon black powder, carbon fiber paper consisting of carbon black powder, carbon nanotube film, graphene film, and other carbon-based materials that have mesoporous structure and good electrical conductivity. In one embodiment, the substrate is a carbon fiber paper.

[0036] The method of the present disclosure is facile, cost effective, and scalable.

[0037] In another aspect, a membrane electrode for use in proton-exchange membrane electrolyzer is provided. The membrane electrode comprises a porous substrate and ruthenium oxychloride species having a general formula RuOCl_y dispersed in a manganese oxide support having a general formula MnO_x , wherein the ruthenium oxychloride species and the manganese oxide support are dispersed within the porous substrate. In various embodiments,

y represents a number of 0.2 to 1.6, and x represents a number 1.7 to 1.8. In one embodiment, the substrate is a carbon fiber paper.

[0038] To facilitate a better understanding of the invention, the following examples of specific embodiments are given. In no way should the following examples be read to limit or define the entire scope of the invention. One skilled in the art will recognize that the examples set out hereinbelow are not an exhaustive list of the embodiments of this invention.

EXAMPLES

Example 1 – Preparation of ruthenium-based electrocatalyst

[0039] In this example, a carbon fiber paper (CFP) was used as the substrate. One will appreciate that other types of substrates can be used without departing from the scope of the present disclosure.

[0040] Firstly, the carbon fiber paper was prepared before use. The carbon fiber paper was sequentially cleaned using ultrasonication by acetone, ethanol, and deionized water, followed by hydrophilic treatment through heating at 250°C for 30 min before use.

[0041] RuOCl@MnO_x sample was fabricated via a one-step heating treatment method by first dissolving 0.5mg of RuCl₃·xH₂O powder and 15 µl of 2.15 M Mn(NO₃)₂ solution in 1 ml deionized water by stirring at room temperature to form a precursor solution. The precursor solution containing ruthenium (III) chloride (RuCl₃) and manganese (II) nitrate (Mn(NO₃)₂) was then added dropwise onto the surface of a 1 cm² carbon fiber paper which was first heated on a hot plate at 210°C. The carbon fiber paper loaded with the precursor solution was then heated at 210°C for another 10 min before being thoroughly rinsed with water. About 46% of the solution (by comparing mass increments between the carbon fiber paper substrate and underlying quartz spacer after heating deposition) was deposited onto carbon fiber paper substrate due to its porous structure and hydrophilic surface. This corresponds to a loading mass of 0.23 mg cm⁻² RuCl₃·xH₂O precursor on the carbon fiber paper. A ruthenium-based

electrocatalyst comprising RuOCl_y species dispersed in MnO_x support ($\text{RuOCl}@ \text{MnO}_x$) was thus obtained. The carbon fiber paper substrate loaded with the ruthenium-based electrocatalyst is suitable for fabrication of membrane electrode assembly in PEM electrolyzer owing to its excellent resistance to acid and oxidation. Notably, this fabrication method is scalable as the method uses mild synthesis conditions and low cost manganese oxide (MnO_2) as the support.

[0042] The schematic electrocatalyst structure is illustrated in FIG. 2 which shows that the ruthenium oxychloride (RuOCl_y) species are dispersed in the manganese oxide (MnO_x) support.

[0043] Individual $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ solution or $\text{Mn}(\text{NO}_3)_2$ solution dropped onto substrate was also prepared using the same heating method to obtain RuOCl or MnO_x control sample, respectively. $\text{RuOCl}/\text{MnO}_x$ serving as another control sample was also fabricated by dropwise addition of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ solution onto as-prepared MnO_x sample following the same heating procedure.

[0044] For the commercial RuO_2 catalyst sample, 4 mg RuO_2 was added to 1 ml of water/ethanol (3:1, v/v) containing 20 μl Nafion solution (5%, DuPont D520), and dispersed by sonication for 1 h to generate homogenous ink. Then 38 μL ink was added dropwise into 1 cm^2 carbon fiber paper substrate to reach a RuO_2 loading mass of 0.15 mg (denoted as $\text{RuO}_2|0.15@ \text{CFP}$), which corresponds to the same Ru atomic mass as that in $\text{RuOCl}@ \text{MnO}_x$, and dropping-drying cycles gave a higher loading mass, denoted as $\text{RuO}_2|x@ \text{CFP}$ ($x=0.15, 0.3, 0.45, 0.6, 0.75, 0.9, 1.05$). In addition, 0.15 mg (38 μL) RuO_2 was dropped to as-synthesized MnO_x to denote carbon fiber paper loaded $\text{RuO}_2/\text{MnO}_x$ working electrode.

Example 2

[0045] The dispersion characteristics, elemental valence, and degree of segregation of ruthenium atoms, as well as the degree of crystallization and particle morphology of the support oxide were investigated using various characterization tools.

[0046] X-ray diffraction (XRD) analysis was performed, and the results are as shown in FIG. 3. The structure analysis from XRD indicates the amorphous states of (A) RuOCl@MnO_x and (C) RuOCl, as suggested by the lack of well-defined peaks. XRD peaks located at $2\theta = 33.1, 55.2, \text{ and } 66.0^\circ$ for (B) MnO_x correspond to (222), (440), and (622) planes of Mn₂O₃ structure, respectively. The absence of crystalline peak in (A) RuOCl@MnO_x suggests that the added ruthenium disturbs the crystallinity of the MnO_x support which is attributed to the disordered bonding and doped/chemisorbed Cl atom. It is worth noting that crystal defects and unsaturated coordination sites in RuO₂ catalyst are responsible for the highly active oxygen evolution reaction. The Raman spectra in FIG. 4 show that the peak positions of (A) RuOCl@MnO_x are close to those of (B) MnO_x, where 505 cm⁻¹, 566 cm⁻¹ (Mn-O stretching vibration in the basal plane), and 643 cm⁻¹ (symmetric stretching mode of the MnO₆ group) correspond to the lattice vibration modes of MnO₂. The (C) RuOCl sample does not show the lattice vibration peaks as those observed in crystalline RuO₂. It is therefore not possible to form crystalline RuO₂ from aqueous ruthenium (III) chloride (RuCl₃) precursor by treatment at 210°C for 10 min, whereas crystalline MnO_x is obtained by pyrolysis of Mn(NO₃)₂ under this condition.

[0047] Elemental compositions analyses were conducted by X-ray photoelectron spectroscopy (XPS) for Ru 3p, Cl 2p, Mn 2p, and O 1s states. The XPS full spectrum in FIG. 5 covers Ru, O and Cl elements in catalysts (A) RuOCl@MnO_x and (B) RuOCl, as well as Mn, O elements from (C) MnO_x support. Ru 3p peaks (FIG. 6) located at 463.8 and 486.2 eV, as well as Ru 3d peaks (FIG. 7) located at 281.3 and 285.5 eV, are assigned to Ru⁴⁺ state. It is noted that the intensity of Ru in RuOCl@MnO_x is much weaker than that in RuOCl even at

the same Ru loadings, indicating its adequate dispersion of Ru element into the MnO_x matrix. Notably, a significant Cl signal (FIG. 8), located at 198.1 eV and 199.8 eV corresponding to Cl $2p_{3/2}$ and Cl $2p_{1/2}$ of Cl^{4+} , was observed in both (A) RuOCl@MnO_x and (B) RuOCl . The Cl could not be completely removed although the prepared sample underwent thorough washing, suggesting that the Cl element has been doped or chemically adsorbed strongly onto the electrocatalyst body or micropores.

[0048] In addition, the O 1s spectra (FIG. 9) can be deconvoluted as the lattice oxygen (529.7 eV), hydroxyl groups/C-O/adsorbed oxygen on surface (531.2 eV).

[0049] The Mn $2p_{3/2}$ signals (FIG. 10) located at 641.7 eV and 643.6 eV in (A) RuOCl@MnO_x and (B) MnO_x are assigned to Mn^{3+} and Mn^{4+} states, respectively, with a ratio of approximately 1.8 ($\text{Mn}^{3+}:\text{Mn}^{4+}$) in RuOCl@MnO_x . The Ru:Cl:O:Mn ratio (1:0.8:15.5:7.8) in RuOCl@MnO_x was obtained by semi-quantitative analysis of XPS (FIG. 11), which reveals that each Ru catalytic site is surrounded by 8 Mn atoms to ensure its good dispersion. In contrast, Cl content is significantly less in RuOCl , which has a ratio of 1:0.2:2.1 for Ru:Cl:O, suggesting that some Cl would be doped or chemisorbed into MnO_x . The Mn:O ratio in MnO_x is (1:1.8) which implies a mixture of polycrystalline Mn_2O_3 and amorphous MnO_2 in MnO_x support, combined with XRD analysis.

[0050] K-edge XANES spectra are analyzed to further confirm the oxidation states of Ru and Mn by fitting the Ru/Mn oxidation states as a function of Ru/Mn K-edge energy shifts (FIG. 12), and the calculated average valence states of Ru and Mn are $\text{Ru}^{+3.9}$ and $\text{Mn}^{+2.8}$, respectively.

[0051] The high-resolution TEM (HRTEM) image in FIG. 13(a) shows that RuOCl@MnO_x is composed of amorphous nanoparticles with tiny nanocrystals, and the d-spacing of 0.27 nm corresponds to (222) plane of Mn_2O_3 . Besides, the SAED patterns obtained and as shown in FIG. 13(b) show faint diffraction rings corresponding to (222),

(411), (521) and (622) planes of Mn_2O_3 , further illustrating the polycrystalline and amorphous composition of RuOCl@MnO_x . The absence of RuO_2 nanocrystal indicates the great dispersion of Ru in the MnO_x support. Furthermore, the image taken by aberration-corrected high-angle annular dark-field STEM (FIG. 13(c)) shows that some individual Ru atoms, as distinguishable bright spots marked by circles, are well dispersed over the surface of the MnO_x support. The element distributions in RuOCl@MnO_x were obtained from scanning STEM-EDS (TEM energy dispersive X-ray spectroscopy) images, and the results as shown in FIGs. 13(d)-(h) show that all elements including Ru, Cl, O, and Mn exhibit uniform distributions in the electrocatalyst. The Fourier transforms (FTs) of the Ru K-edge $k^2\chi(k)$ spectra (FIG. 13(i)) show the Ru-O peak shifts to 1.57 Å of (A) RuOCl@MnO_x from 1.50 Å of (B) RuO_2 , which is attributed to the change in the local coordination environment due to the dominance of Ru-O-Mn bonds in RuOCl@MnO_x . The absence of Ru-Cl peak indicates the complete conversion of Ru-Cl to Ru-O during the thermal synthesis. The Fourier transforms (FTs) of the Mn K-edge $k^2\chi(k)$ spectra as shown in FIG. 13(j), where 1.5, 2.4 and 3.0 Å match the Mn-O bond, edge-sharing Mn-Mn_{edge}, and corner-sharing Mn-Mn_{corner} in the MnO_6 octahedra, respectively, suggest that the MnO_6 octahedra framework in the MnO_x support is maintained despite the introduction of external elements, in accordance with the Raman results. The missing Ru-Cl and Mn-Cl bonds above agree with the doping or adsorption state of Cl in the catalyst. In addition, the EELS pattern as shown in FIG. 14 shows only the signals of Mn and O in the sample RuOCl@MnO_x , in contrast to the obvious Ru and Cl peaks in RuOCl . The absence of Ru and Cl peaks due to the weakening of the signal caused by the encapsulation of manganese oxide support suggest that RuOCl has been dispersed uniformly in the MnO_x matrix rather than segregate on the surface. SEM images as shown in FIG. 15 indicate that both RuOCl@MnO_x and MnO_x are densely deposited on the carbon fiber paper (CFP) surface, however, RuOCl shows poor coverage. SEM-EDS analysis

was also employed to quantify the content of elements and the results are as shown in FIG. 16. The results suggest that Ru, Cl, O, Mn are uniformly distributed on the deposited membrane. The Ru:Cl:O:Mn (1:1.6:18.0:11.1) ratios in RuOCl@MnO_x (see FIG. 13(k) for spectrum) and the Ru:Cl:O (1:0.4:2.4) ratios in RuOCl (see FIG. 13(l)) obtained from EDS suggest that the percentage of Cl element by EDS is higher than that by XPS, indicating more Cl has been doped or chemisorbed beneath the surface. Furthermore, the Mn:O (1:1.7) ratio measured by EDS is close to that obtained by XPS spectra, suggesting a mixture of polycrystalline Mn₂O₃ and amorphous MnO₂. The mass loading of Ru in RuOCl@MnO_x is 0.112 mg cm⁻² (calculated as molecular weight = 207.43 g mol⁻¹ for RuCl₃·H₂O) or 0.105 mg cm⁻² [based on inductive coupled plasma (ICP) testing], corresponding to 0.15 mg or 0.14 mg pristine RuO₂, respectively.

Example 3

[0052] ICP-OES results of the prepared RuOCl@MnO_x were obtained. A piece of CFP-loaded RuOCl@MnO_x (1 cm²) was placed into 10 mL concentrated hydrochloric acid at 60°C for 20 min, and then the solution was transferred to a 250-mL volumetric flask for quantification with 0.23 mol L⁻¹ nitric acid. The blank sample with pure CFP was subjected to the same treatment. The results are as shown in Table 1.

Table 1

ions	Ru / mg L ⁻¹	Mn / mg L ⁻¹
	0.419	2.192

[0053] ICP-OES results of the electrolytes (50 mL) after 280-h, 200-h, 100-h, and 50-h chronopotentiometry tests at 10, 100, 300, and 500 mA cm⁻², respectively were obtained. The acidity was adjusted with 0.23 M nitric acid and the ionic concentration was converted to be similar to that dissolved in the original electrolyte. The blank sample was subjected to the

same treatment, except that no chronopotentiometry test was performed. The results are as shown in Table 2.

Table 2

Ions dissolved in electrolyte	Working electrode area	Ru / mg L ⁻¹	Mn / mg L ⁻¹
10 mA cm ⁻² for 280 h	1 cm ²	1.405	1.502
100 mA cm ⁻² for 200 h	1 cm ²	1.469	1.685
300 mA cm ⁻² for 100 h	0.5 cm ²	0.857	0.982
500 mA cm ⁻² for 50 h	0.5 cm ²	1.004	1.275

[0054] Deposition of Ru on cathodic Pt wire was observed after long-term test, and the Ru was returned to solution by applying a high voltage (2 V) for a short time (30 s) to obtain a shiny Pt wire and more accurate ion concentrations. Notably, the Ru deposited on the cathode Pt has no significant effect on the anodic oxygen evolution reaction process studied here.

[0055] The ICP-OES also gives the ratio of Ru:Mn (1:9.6) in RuOCl@MnO_x, which is close to that estimated from EDS or XPS analysis. Table 3 is a summary of atomic ratios obtained from XPS/EDS/ICP-OES, where the atomic concentrations are normalized to that of Ru in the RuOCl@MnO_x and RuOCl samples, and to that of Mn in MnO_x.

Table 3

Atomic ratio	RuOCl@MnO _x				MnO _x		RuOCl		
	Ru	Mn	O	Cl	Mn	O	Ru	O	Cl
XPS	1	7.8	15.5	0.8	1	1.8	1	2.1	0.2
EDS	1	11.1	18.0	1.6	1	1.7	1	2.4	0.4
ICP-OES	1	9.6							

Example 4

[0056] Electrochemical tests were carried out to evaluate stability and activity of the electrocatalyst of the present disclosure.

[0057] Electrochemical performance tests were carried out on an electrochemical workstation (CHI 660E) with a standard three-electrode setup in an electrolyte of 0.5 M H₂SO₄ after purging with O₂. Carbon fiber paper loaded RuOCl@MnO_x, RuOCl, MnO_x, RuOCl/MnO_x, RuO₂/MnO_x, and RuO₂|x@CFP samples were used as the working electrodes. An Ag/AgCl (saturated KCl) electrode and a Pt wire were used as the reference electrode and counter electrode, respectively. All LSV (linear sweep voltammetry) curves were recorded with the potential sweep rate at 5 mV s⁻¹, and chronopotentiometric measurements were performed at 10 mA cm⁻², 100 mA cm⁻², 300 mA cm⁻², and 500 mA cm⁻², respectively. The geometric areas used for electrochemical LSV testing, 10 and 100 mA cm⁻² chronopotentiometric measurements were 1 cm², and the areas used for 300 and 500 mA cm⁻² chronopotentiometric measurements were 0.5 cm². Test areas of LSV curves extended to high anodic potential for CFP-loaded RuO₂|0.15@CFP, RuOCl@MnO_x and MnO_x were 1, 0.5 and 0.5 cm², respectively, and the potential scan rate was 0.1 mV s⁻¹. All potentials, with full iR correction (manual iR compensation, where R_s was obtained from EIS result under open-circuit voltage) if not mentioned separately, were converted to a reversible hydrogen electrode (RHE) scale, *i.e.*, $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.197 \text{ V} + 0.059 \times \text{pH}$.

[0058] Stability test was conducted, and the results are as shown in FIG. 17(a), which shows the potential change at a constant oxygen evolution reaction current density of 10 mA cm⁻². The RuOCl@MnO_x catalyst displays stable operation up to 280 h with only 50 mV overpotential decrease corresponding to a degradation rate of 0.18 mV h⁻¹ (see curve A). Notably, most of the degradation (46%) occurs in the first 25 h (the inset of FIG. 17(a)). This superior stability outperforms most ruthenium-based oxygen evolution reaction electrocatalyst operation in acidic media. In contrast, both pristine RuO₂ and RuOCl exhibit rapid activity decay. Specifically, (D) RuO₂|1.05@CFP and (E) RuO₂|0.15@CFP (with 1 and 7 times as much Ru mass loading as that in RuOCl@MnO_x, respectively) completely deactivated in 10 h

and 0.05 h, respectively. Meanwhile, the potential of (B) RuOCl increases from 1.44V to 2V in 4 h, corresponding to a degradation rate of 140 mV h⁻¹. Moreover, the relatively steady oxygen evolution reaction potential of (C) MnO_x decayed from 1.86 V to 1.93 V within 20 h. This discloses its strong antioxidant capability, but inferior oxygen evolution reaction activity. These comparative data suggest that Ru is the active site and MnO_x acts as the supporting material, endowing RuOCl@MnO_x with superior stability and activity. In addition, it is noted that the potentials of (F) RuOCl/MnO_x and (G) RuO₂/MnO_x underwent much slower decrease to 1.54 V and 1.79 V in 30 h and 20 h, respectively, in contrast to the rapid deactivation of (B) RuOCl (in 4 h) and (E) RuO₂|0.15@CFP (in 0.05 h), signifying that MnO_x also stabilizes the electrocatalyst even by simple loading on its surface. The enhanced durability of RuOCl/MnO_x and RuO₂/MnO_x could be ascribed to the valence state and structural transformation of MnO_x during the oxygen evolution reaction process. However, the inhomogeneous and uncontrollable dynamic surface reactions make RuO₂/MnO_x less active than RuOCl@MnO_x.

[0059] It is to be noted that the term “RuOCl/MnO_x” as used herein refers to ruthenium oxychloride (RuOCl) species dispersed in manganese oxide (MnO_x) support wherein no chemical bonding is formed between the RuOCl species and the MnO_x support.

[0060] The term “RuO₂/MnO_x” as used herein refers to RuO₂ species dispersed in manganese oxide (MnO_x) support wherein no chemical bonding is formed between the RuO₂ species and the MnO_x support.

[0061] Steady oxygen evolution reaction operation at high current densities accelerates the oxidative failure of the electrocatalyst and thus it is an important consideration in practical applications. The stability of the electrocatalyst was tested at higher current densities, at 100 mA cm⁻², 300 mA cm⁻² and 500 mA cm⁻². The results are as shown in FIG. 17(b). After 200-h continuous operation at 100 mA cm⁻², the overpotential increment is 115 mV. This

corresponds to a degradation rate of 0.6 mV h^{-1} . The degradation accelerates at 300 mA cm^{-2} (at a degradation rate of 164 mV in 100 h) and 500 mA cm^{-2} (at a degradation rate of 346 mV in 50 h).

[0062] Next, the activity of the electrocatalyst RuOCl@MnO_x was evaluated using linear scanning voltammetry (LSV) curves (FIG. 17(c)). RuOCl@MnO_x exhibits excellent activity with an onset potential of 1.42 V (and an overpotential of only 228 mV at 10 mA cm^{-2}). In contrast, the onset potentials of (C) $\text{RuO}_2|0.15\text{@CFP}$ and (D) $\text{RuO}_2|1.05\text{@CFP}$ are much higher at 1.52 V and 1.48 V , respectively. The overpotential of $\text{RuO}_2|1.05\text{@CFP}$ is 306 mV at current density of 10 mA cm^{-2} (FIG. 18). $\text{RuO}_2|1.05\text{@CFP}$ and $\text{RuO}_2|0.15\text{@CFP}$ show small current densities of 32 and 5 mA cm^{-2} (vs. 118 mA cm^{-2} of RuOCl@MnO_x) at 1.6 V . Moreover, the high onset potential of 1.77 V and high overpotential of 620 mV at 10 mA cm^{-2} for MnO_x also indicate that the active site is not derived from MnO_x support. In addition, RuOCl suffered a rapid decay in the potential scan test (FIG. 19). It is noted that $\text{RuO}_2|0.15\text{@CFP}$ with the same Ru mass loading as that of RuOCl@MnO_x (calculated as molecular weight = $207.43 \text{ g mol}^{-1}$ for $\text{RuCl}_3 \cdot \text{H}_2\text{O}$) has a much higher overpotential than 306 mV in driving a current density of 10 mA cm^{-2} . Upon gradual increase of Ru loading (see FIG. 20(a)), the overpotential of $\text{RuO}_2|1.05\text{@CFP}$ reaches 306 mV , close to that of RuO_2 (approximately 0.275 mg cm^{-2}) loaded on a glassy carbon electrode. Such inferior performances are attributed to the loaded RuO_2 nanoparticles (TEM image in FIG. 20(b)) partially trapped in the interfibrillar voids in the carbon fiber paper, and thus could not participate in catalytic reaction efficiently. The mass activity (FIG. 21) of (A) RuOCl@MnO_x is as high as $481 \text{ A g}_{\text{Ru}}^{-1}$ at $\eta = 300 \text{ mV}$, which is 41 higher than that of (C) $\text{RuO}_2|1.05\text{@CFP}$ or (B) $\text{RuO}_2|0.15\text{@CFP}$ (FIG. 18), suggesting that it is one of the most superior low-mass-loading Ru-based and Ir-based electrocatalysts. Notably, referring to FIG. 22, the Tafel curves of (A) RuOCl@MnO_x (43 mV dec^{-1}) is smaller than that of (B) $\text{RuO}_2|1.05\text{@CFP}$ (48 mV dec^{-1}).

¹) and (C) RuO₂|0.15@CFP (53 mV dec⁻¹), indicating faster oxygen evolution reaction kinetic.

[0063] The structural stability of the electrocatalyst was examined after 280-h stability testing was carried out. Compared with the initial rough and dense membranes (see FIG. 23(a)-(c)), the electrocatalyst appears to resemble a nanosheet structure of MnO₂ after the stability test (see FIG. 23(d)-(f)). The Raman peaks are slightly shifted to 497 cm⁻¹, 572 cm⁻¹, 651 cm⁻¹, as shown in FIG. 26(a), which may originate from the change of valence state and bond length. The newly appeared peak located at 385 cm⁻¹ corresponds to the bending mode of Mn-O-Mn. However, the XRD pattern in FIG. 24 does not show any crystalline MnO₂ peak, which suggests a predominantly amorphous phase of MnO₂. It is still possible to observe some tiny nanocrystals with a lattice spacing of 0.36 nm by HRTEM (FIG. 25), which corresponds to the (002) plane of δ -MnO₂, suggesting the transformation of the MnO_x support during the catalysis process. The XPS and normalized Ru K-edge XANES spectra of RuOCl@MnO_x after 48-h testing (FIG. 26(b-c)) show no significant degradation of Ru active site in the early stage of long-term catalysis. The Mn K-edge XANES spectra shift from an energy close to Mn₂O₃ (Mn³⁺ reference) towards that of MnO₂ (Mn⁴⁺ reference) after 48-h testing, while a significant positive shift of the Mn 2p peak is observed after 280 h by XPS (see FIG. 26(d)-(e)). Concurrently, the Mn³⁺/Mn⁴⁺ ratio gradually decreases from 1.8 (initial) to 1.1 (after 280 h), further indicating an increase of MnO₂, which is consistent with the morphological and Raman characterizations. Doped/chemisorbed Cl (FIG. 26(f)) is closely related to the degradation of the electrocatalyst. With the Cl peak disappears after 280-h test, apparent degradation occurs after 280 h. In addition, the O 1s peak (FIG. 27(a)) of lattice oxygen shifts slightly after 280-h test, which could be attributed to the composition, valence state, and microstructure of the re-deposited MnO₂ nanosheet. The weight of Mn and Ru ions dissolved in solution after 280-h stability testing is 0.08 mg and 0.07 mg, respectively. Other

dissolved Mn^{3+} , however, is redeposited on the surface in the form of MnO_2 nanosheets (see FIG. 23 and FIG. 25). Notably, the high activity of the electrocatalyst was not significantly affected during the re-deposition process, and the Faradaic efficiency (electric charges involved) of Mn/Ru ionic reactions is negligible compared to those of oxygen evolution reaction or hydrogen evolution reaction (HER). Moreover, sheet-like structures with morphological variation depending on the applied potentials are also observed after stability tests at high current densities. FIG. 28 are SEM images and SEM-EDS full element mappings of RuOCl@MnO_x after (a-c) 200-h stability test at 100 mA cm^{-2} , after (d-f) 100-h stability test at 300 mA cm^{-2} , and after (g-i) 50-h stability test at 500 mA cm^{-2} . The flakes are dominated by amorphous phase, as shown by the HRTEM images of RuOCl@MnO_x as shown in FIG. 29. The Raman peaks as shown in FIG. 30 exhibit slight shift, accompanied by appearance of peaks located at 385 cm^{-1} (bending vibration of Mn-O-Mn) and 720 cm^{-1} (stretching vibration of Mn-O-Mn). Additionally, the Ru 3p peaks are significantly weakened, and both Mn 2p and O 1s peaks show similar positive shifts (see FIG. 31). The Mn and Ru ions undergo more rapid dissolution at high anodic potentials, as revealed by ICP-OES characterization (see Table 3).

[0064] MnO_2 and RuO_2 corrode via the following reactions:

[0065] $\text{MnO}_2 + 2\text{H}_2\text{O} \rightarrow \text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^-$ ($E^0 = 1.70 \text{ V vs. RHE}$), and

[0066] $\text{RuO}_2 + 2\text{H}_2\text{O} \rightarrow \text{RuO}_4(\text{aq}) + 4\text{H}^+ + 4\text{e}^-$ ($E^0 = 1.39 \text{ V vs. RHE}$).

[0067] For the durability test, the MnO_x catalyst support in the present disclosure remains stable for at least 20 h in the range of 1.86 to 1.93 V (FIG. 17(a), curve C). The calculated Pourbaix diagram (FIG. 32) of 89-11% Mn-Ru system in aqueous solution also demonstrates a higher oxidation potential of MnO_2 than RuO_2 . Slow scan (0.1 mV s^{-1}) LSV experiment extended to high anodic potentials was also performed, and the results are as shown in FIG. 33. The results show that the oxygen evolution reaction dominates prior to catalyst

degradation, and significant degradation occurs at the clear inflection points of oxygen evolution reaction current. For $\text{RuO}_2|0.15\text{@CFP}$, RuOCl@MnO_x , and MnO_x , the potentials at the inflection points are 1.76 V, 2.49 V, and 2.55 V, respectively. One can see that the MnO_x support greatly improves the oxidation potential of the RuOCl@MnO_x electrocatalyst. It is noteworthy that the elevated oxidation potential is crucial for enhancing stability. The dissolution of RuO_2 lattice, which is triggered by the loss of lattice/surface oxygen accompanied by the sharing of oxygen evolution reaction intermediates, depends on the applied potential, and it becomes more severe when the potential is much higher than the theoretical redox potential (1.39 V_{RHE} , pH 0). The dispersion of Ru into MnO_x support results in high oxidation potential of the electrocatalyst and therefore able to achieve long-term stability even at high current density.

[0068] In view of the predominantly amorphous characteristic of the electrocatalyst, catalytic reaction may involve the participation of lattice/surface oxygen. Distinct from the Ru-O-Ru bonding in conventional RuO_2 , Ru-O-Mn bonding dominates here (FIG. 13(i)) as a Ru atom is surrounded by up to ten times more Mn atoms. Due to the difference in bond length, electronegativity, and bond strength between Mn-O and Ru-O, the RuOCl@MnO_x electrocatalyst differs from RuO_2 in terms of recovery of catalyst structure such as oxygen vacancy. The oxygen vacancies involving lattice/surface oxygen accelerate the dissolution of RuO_2 , while the enhanced stability of Ru catalyst is attributed to the presence of MnO_x that could promote the recovery of structure and thus reduce catalyst degradation. Thus, the bulk formation energy and surface energy for the three models of RuO_2 , Mn_2O_3 , and $\text{Mn}_2\text{O}_3\text{Ru}$ (see FIG. 34) were calculated since formation energy and surface energy are key parameters to assess the structural stability.

[0069] The surface energy (E_{sur}) and formation energy (E_{form}) were calculated by the following equations (1) and (2):

$$[0070] \quad E_{sur} = \frac{1}{2A} (E_{surface} - nE_{bulk}) \quad (1)$$

$$[0071] \quad E_{form} = \frac{1}{n_M + n_O} (nE_{bulk} - n_M E_M - n_O E_O) \quad (2)$$

where E_{bulk} is the total energy per unit cell of the bulk, n is the number of unit cells that the slab model contains, and A is the surface area of the slab model. E_M is the bulk energy of per metal atom. E_O is half of oxygen energy. n_M and n_O are the number of metal and oxygen atom in bulk system, respectively.

[0072] It is worth noting that Mn_2O_3 was appropriate as the simulation model for the MnO_x support based on the experimental XRD, HRTEM, XPS and Mn K-edge XANES analyses, which show Mn^{3+} is dominant. Moreover, the doped/chemisorbed Cl was not included in the model because it is not directly involved in the oxygen evolution reaction process. As depicted in FIG. 33(b), the formation energies of RuO_2 , Mn_2O_3 and Mn_2O_3Ru are -1.16 eV, -1.61 eV and -1.54 eV, while the surface energies are 1.30 eV, 0.65 eV and 0.73 eV, respectively. Notably, both bulk formation energy and surface energy of Mn_2O_3 are lower than those of RuO_2 , suggesting Mn_2O_3 is more stable than RuO_2 . Moreover, it suggests that even 9% Mn are substituted by Ru (*i.e.*, Mn_2O_3Ru), the energy is still lower than that of RuO_2 , which signifies the greatly enhanced structural stability of Mn_2O_3Ru than pure RuO_2 .

[0073] The calculated Gibbs free energy during oxygen evolution reaction process on different surfaces are displayed as shown in FIG. 33(c) to evaluate the intrinsic activity. Here, simulation models of Mn_2O_3Ru with 9% Ru close to experimentally measured value, as well as RuO_2 were constructed as reference, as exhibited in FIG. 33(d). Ruthenium serving as surface catalysis center has unsaturated coordination structure, where Ru in RuO_2 and Ru1 in Mn_2O_3Ru have five-coordinated structure and Ru2 in Mn_2O_3Ru has four-coordinated structure, and these unsaturated sites are analogue to the lattice/surface oxygen vacancies for catalysis (FIG. 35). Adsorbate evolution mechanism (AEM) is considered in the present disclosure. The energy of oxygen in ideal catalysis process is estimated as $\Delta G_{O_2} = 4 \times 1.23 =$

4.92 eV since it is a four-electron-transfer process. Comparing the Gibbs free energy on different surfaces, the reaction process of Ru2 site on $\text{Mn}_2\text{O}_3\text{Ru}$ (110) surface is closer to ideal catalysis process than pure RuO_2 and Ru1 site on $\text{Mn}_2\text{O}_3\text{Ru}$ (110) surface, since the theoretical overpotentials for Ru2 site on $\text{Mn}_2\text{O}_3\text{Ru}$ (110), RuO_2 , Ru1 site on $\text{Mn}_2\text{O}_3\text{Ru}$ (110), and Mn site on $\text{Mn}_2\text{O}_3\text{Ru}$ (110) surfaces are 0.75, 0.99, 1.11, and 1.32 V, respectively. The formation of O^* from OH^* serves as the rate-determining step (RDS) for the four-coordinated Ru2 site bearing a low overpotential, although it is still higher than the experimental overpotential because the effects of solution and temperature are not taken into account in modelling. As a contrast, the five-coordinated Ru1 site is limited by the formation of O_2 from OOH^* , accompanied by a larger overpotential than RuO_2 . The largest overpotential of the Mn site also illustrates its role as a supporting material. Overall, the increase in activity is related to the four-coordinated unsaturated structure of Ru in the RuOCl@MnO_x catalyst.

[0074] In the present disclosure described hereinabove, a stabile ruthenium-based electrocatalyst is obtained by dispersing catalytically active RuOCl species into a low-cost MnO_x support to obtain a cost-effective, active, and stable oxygen evolution reaction electrocatalyst for use in acidic electrolyte. In an exemplary embodiment, the electrocatalyst delivers 10 mA cm^{-2} at an overpotential of 228 mV, a mass activity of $481 \text{ A g}_{\text{Ru}}^{-1}$ at overpotential of 300 mV, and a Tafel slope of 43 mV dec^{-1} . More importantly, it exhibits excellent stability for 280 hours at 10 mA cm^{-2} , far exceeding that of pristine RuO_2 or support-free RuOCl catalyst. Stable operation over 200, 100, and 50 hours at 100, 300, and 500 mA cm^{-2} , respectively, have been demonstrated. Combining synchrotron radiation and other characterizations, the outstanding stability is attributed to the synergistic effect of the catalytic species and the support, where the MnO_x support with high resistance to acid and oxidation increases the oxidation potential and slows down the oxidative corrosion of ruthenium, while the Ru active sites allow oxygen evolution reaction to occur at low

potentials which in turn, suppresses corrosion of MnO_x support. The dispersion of RuOCl into MnO_x support increases oxidation potential and lowers bulk formation and surface energies. As a result, the durability of the electrocatalyst is drastically enhanced. Notably, four-coordinated Ru site in the catalyst bears a lower overpotential and thus higher activity than pure RuO_2 catalyst. The ruthenium-based electrocatalyst of the present disclosure and the method for preparing the same offer a new strategy for making stable and active oxygen evolution reaction electrocatalyst with low ruthenium loading for PEM electrolyzer.

CLAIMS

1. A ruthenium-based electrocatalyst comprising:
ruthenium oxychloride species having a general formula RuOCl_y dispersed in a manganese oxide support having a general formula MnO_x .
2. The ruthenium-based electrocatalyst according to claim 1, wherein y represents a number of 0.2 to 1.6, and x represents a number 1.7 to 1.8.
3. The ruthenium-based electrocatalyst according to claim 2, wherein the ruthenium oxychloride species are chemically bonded to the manganese oxide support.
4. The ruthenium-based electrocatalyst according to claim 3, wherein the ruthenium-based electrocatalyst is $\text{RuOCl}@\text{MnO}_x$.
5. The ruthenium-based electrocatalyst according to claim 1, wherein the molar ratio of RuOCl_y to MnO_x is 1:11.1 or 1:7.8.
6. The ruthenium-based electrocatalyst according to claim 1, wherein the Ru:Cl:O ratio in RuOCl is 1:0.4:2.4 or 1:0.2:2.1.
7. The ruthenium-based electrocatalyst according to claim 1, wherein the Mn:O ratio in MnO_x is 1:1.7 or 1:1.8.
8. The ruthenium-based electrocatalyst according to claim 1, further comprising carbon black powder dispersed in the manganese oxide (MnO_x) support.

9. The ruthenium-based electrocatalyst according to any one of claims 1 to 8, further comprising a substrate, wherein the ruthenium oxychloride species and the manganese oxide support are dispersed within the substrate.
10. The ruthenium-based electrocatalyst according to claim 9, wherein the substrate is selected from the group consisting of carbon fiber paper, carbon cloth, carbon cloth covered by a thinner microporous layer consisting of carbon black powder, carbon fiber paper consisting of carbon black powder, macroporous carbon fiber paper, carbon nanotube film and graphene film.
11. The ruthenium-based electrocatalyst according to claim 10, wherein the substrate is a carbon fiber paper.
12. A method of preparing a ruthenium-based electrocatalyst, the method comprising:
heating a substrate;
adding a precursor solution containing a chloride salt of ruthenium and a nitrate salt of manganese onto the substrate; and
heating the precursor solution with the substrate to obtain a ruthenium-based electrocatalyst comprising ruthenium oxychloride species having a general formula RuOCl_y dispersed in a manganese oxide support having a general formula MnO_x .
13. The method according to claim 12, wherein the precursor solution and the substrate are heated at a temperature ranging from 200°C to 220°C.

14. The method according to any one of claim 12 or 13, wherein y represents a number of 0.2 to 1.6, and x represents a number 1.7 to 1.8.
15. The method according to claim 12, wherein the ruthenium oxychloride species and the manganese oxide support are dispersed within the substrate.
16. The method according to claim 15, wherein the substrate is selected from the group consisting of carbon fiber paper, carbon cloth, carbon cloth covered by a thinner microporous layer consisting of carbon black powder, carbon fiber paper consisting of carbon black powder, macroporous carbon fiber paper, carbon nanotube film and graphene film.
17. The method according to claim 16, wherein the substrate is a carbon fiber paper.
18. A membrane electrode for use in a proton-exchange membrane electrolyzer comprising:
a substrate, and ruthenium oxychloride species having a general formula RuOCl_y dispersed in a manganese oxide support having a general formula MnO_x , wherein the ruthenium oxychloride species and the manganese oxide support are dispersed within the substrate.
19. The membrane electrode according to claim 18, wherein the substrate is a carbon fiber paper.