

SYNTHESIS OF NOBLE METAL SULPHIDE CATALYSTS IN A SULPHIDE ION-FREE AQUEOUS ENVIRONMENT.

FIELD OF THE INVENTION

- 5 The invention is relative to a catalyst, in particular to a noble metal sulphide electrocatalyst and to a method for producing the same.

BACKGROUND OF THE INVENTION

10 Noble metal chalcogenides are widely known in the field of electrocatalysis; in particular, electrocatalysts based on rhodium and ruthenium sulphide are currently incorporated in gas-diffusion electrode structures for use as oxygen-reducing cathodes in highly aggressive environments, such as in the depolarised electrolysis of hydrochloric acid.

15 Noble metal sulphides for use in electrocatalysis are prepared by sparging hydrogen sulphide in an aqueous solution of a corresponding noble metal precursor, usually a chloride, for instance as disclosed in US 6,149,782 which is relative to a rhodium sulphide catalyst. The synthesis of noble metal sulphide catalysts with hydrogen sulphide in aqueous solutions is conveniently carried out in the presence of a conductive carrier, in most of the cases consisting of
20 carbon particles. In this way, the noble metal sulphide is selectively precipitated on the carbon particle surface, and the resulting product is a carbon-supported catalyst, which is particularly suitable for being incorporated in gas-diffusion electrode structures characterised by high efficiency at reduced noble metal loadings. High surface carbon blacks, such as Vulcan XC-72 from Cabot
25 Corp./USA are particularly fit to the scope.

A different procedure for the preparation of carbon-supported noble metal sulphide catalysts consists of an incipient wetness impregnation of the carbon carrier with a noble metal precursor salt, for instance a noble metal chloride, followed by solvent evaporation and gas-phase reaction under diluted hydrogen
30 sulphide at ambient or elevated temperature, whereby the sulphide is formed in a stable phase. This is for instance disclosed in the co-pending provisional application 60/473,543, which is relative to a ruthenium sulphide catalyst.

In the case of rhodium, prior to its use, the noble metal sulphide catalysts so obtained are subjected to an adequate stabilising thermal treatment, at a temperature usually comprised between 300 and 700°C. In other cases, a temperature as low as 150°C may be sufficient for an adequate thermal treatment.

Although these catalysts show good performances in terms of oxygen reduction activity and of stability in highly aggressive environments, that makes them virtually the only viable materials for oxygen reduction catalysis in hydrochloric acid electrolysis, their production via hydrogen sulphide route is affected by some inconveniences.

Firstly, the use of a highly hazardous species such as hydrogen sulphide, which is a flammable and noxious gas, in their synthesis poses serious environmental and human health concerns. The handling of hydrogen sulphide is a very delicate matter which can only be dealt by resorting to expensive safety measures.

Secondly, the precipitation in an environment where free sulphide ions are present can lead to the formation of compounds with variable stoichiometry, and this can hamper the reproducibility of the required catalyst, especially with certain noble metals; sulphide ions are furthermore a toxic and environmentally unfriendly species.

Other common reagents for the precipitation of sulphides, such as polysulphides, thioacetic acid or thioacetamide, are less hazardous than hydrogen sulphide, but the reaction pathway in an aqueous environment still follows a pre-ionisation or hydrolisation of these compounds to provide undesired free sulphide ions.

An alternative synthetic route for the production of noble metal sulphides to be used in oxygen reduction catalysis, in the absence of free sulphide ions and especially of the highly flammable and highly toxic hydrogen sulphide species is therefore a stringent requirement for a successful scale-up of noble metal sulphide catalyst production, and eventually for the commercialisation of potentially large electrochemical processes such as the depolarised electrolysis of hydrochloric acid.

OBJECTS OF THE INVENTION

It is an object of the present invention to provide a noble metal sulphide catalyst, optionally supported on carbon particles, by precipitation in an aqueous environment free of hydrogen sulphide, and essentially free of sulphide ion species.

It is another object of the present invention to provide a method for producing noble metal sulphide catalysts in an aqueous environment avoiding the use of highly flammable and highly toxic species.

DESCRIPTION OF THE INVENTION

Under one aspect, the invention is relative to a noble metal sulphide catalyst, preferably supported on high surface area carbon black, obtained by reacting a correspondent noble metal precursor, preferably a chloride, with a thionic species in an aqueous solution; by high surface area carbon black it is intended a carbon black species with surface area exceeding 50 m²/g. By thionic species, it is intended any chemical species containing a thio function, such as thiosulphates, thionic acids and acid derivatives thereof. In a preferred embodiment, the reaction is carried out in an aqueous solution essentially free of sulphide ions. The catalyst of the invention may be the sulphide of any noble metal or even a mixed sulphide of at least one noble metal and one or more co-elements; in a preferred embodiment, such noble metal is selected from the group of ruthenium, rhodium, platinum, iridium and palladium.

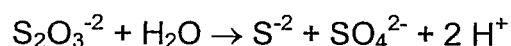
In a most preferred embodiment, the catalyst of the invention is subjected to a thermal treatment at a temperature of 150 to 700°C prior to its use.

The catalyst of the invention is particularly suitable for being incorporated in gas-diffusion electrode structures produced on conductive webs such as carbon cloths or metal meshes, especially gas-diffusion cathodes for oxygen-depolarised electrolysis of hydrochloric acid or other oxygen-consuming cathodes in highly aggressive environments.

Under another aspect, the invention is relative to a method for the production of a noble metal sulphide catalyst in the absence of hydrogen sulphide, and

essentially in a free sulphide ion-free environment, comprising reacting a solution of a precursor of the noble metal, optionally a chloride, with an aqueous solution containing a thionic species, preferably a sodium or ammonium thiosulphate or tetrathionate solution. The noble metal sulphide catalyst of the invention may comprise the sulphide of a single noble metal, or the mixed sulphide of a noble metal and of a further, noble or non noble metals. The precursor solution of noble metal may therefore comprise precursors of further, noble or non noble metals. Alternatively, a mixed sulphide catalyst may be prepared by reacting the precursor solution of a noble metal and a thionic species containing a second, noble or non noble metal.

It is known that, in general, the thiosulphate anion can form sulphides by a disproportionation reaction, giving one sulphide and one sulphate ion as products:

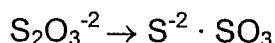


The inventors have nevertheless found out that, in certain conditions, the synthesis of sulphides of noble metals (e.g. rhodium, ruthenium, iridium, platinum or palladium) from thiosulphates proceeds without any detectable release of free sulphide ions.

Without wishing the present invention to be bound to any particular theory, it can be assumed that the process occurs by direct reaction of the metal ion with one of the two sulphur atoms, resulting in the splitting off of the remaining portion.

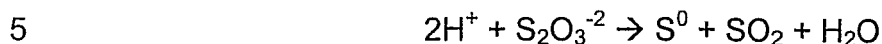
More precisely, in the example reported hereafter, the inventors have observed that the preferred pathway is that of partial disproportionation also known as metathesis of the

$\text{S}_2\text{O}_3^{-2}$ species in which the two S atoms are non equivalent according the following stoichiometry:



The inventors observed in particular that thiosulphates react with some transition metals at pH comprised between 0.1 and 4.0 to form metal sulphides when the aqueous solution containing the reagent is brought to boiling or at temperatures ranging between 50 °C and 100 °C.

When thiosulphates are used for the precipitation of sulphides, the order of addition of the reagents is critical in providing the desired sulphide catalyst. In fact, if thiosulphate were added first to an acidic solution in the absence of the metals to be precipitated, the following disproportionation reaction would occur:



Conversely, if metal ions are present in solution prior to the addition of thiosulphate, the latter appears to be stabilised thus retarding disproportionation and therefore allowing for a metathesis to a sulphide. The order of addition of the reagents is instead less important as concerns other types of thionic species. For instance, tetrathionate is very stable in acidic solution and does not undergo a disproportionation reaction of the kind seen above.

The precipitation of sulphides from other thionic acid derivatives such as dithionate ($\text{S}_2\text{O}_6^{-2}$), trithionate ($\text{S}_3\text{O}_6^{-2}$), tetrathionate ($\text{S}_4\text{O}_6^{-2}$), pentathionate ($\text{S}_5\text{O}_6^{-2}$) or heptathionate ($\text{S}_7\text{O}_6^{-2}$) is not mentioned in the prior art, and its pathway is not yet completely clear. However, the inventors could obtain various noble metal chalcogenides from all of these species, in conditions similar to those relative to the precipitation with thiosulphates, again with no detection of free sulphide ions in any step of the process. The precipitation of noble metal or mixed metal sulphides with a tetrathionate species (for instance with sodium tetrathionate) is particularly preferred, since sodium tetrathionate is a widespread and cheap commercial product. Also in this case, the reaction with transition metals occurs in a pH range comprised between 0.1 and 4.0 (most preferably between 1.0 and 4.0), in a temperature range between 50°C and the boiling temperature.

25 In a preferred embodiment, the reaction is carried out in the presence of high surface area carbon particles or other inert and preferably conductive particles to obtain a supported noble metal sulphide catalyst. In a preferred embodiment, the solution of thionic reactant is added in discrete aliquots, for instance 2 to 10 equivalent aliquots added at time intervals ranging from 15 seconds to 10 minutes. In a preferred embodiment, after adding the solution of thionic reactant to the noble metal precursor solution, the resultant solution is heated to boiling temperature until the reaction is completed (which may take 5 minutes to two

hours, depending on the selected precursor and the reaction conditions). The reaction is preferably followed by colour change of the supernatant liquid, so that completion of the reaction may be simply determined.

In a most preferred embodiment, the method of the invention further comprises
5 subjecting the product thus obtained to a thermal treatment at a temperature of 150 to 700°C prior to its use.

The following examples have the purpose of better clarifying the invention, without constituting a limitation of its scope, which is exclusively defined by the appended claims.

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EXAMPLE 1

Described herein is a method to precipitate rhodium sulphide on carbon from an acidic aqueous solution free of sulphide ions. Precipitation reactions of other noble metal sulphide catalysts (such as the sulphides of ruthenium, platinum,
15 palladium or iridium) only require minor adjustments that can be easily derived by one skilled in the art.

7.62 g of $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ were dissolved in 1 litre of deionised water, and the solution was refluxed (preparation of the noble metal precursor solution).

7 g of Vulcan XC72-R high surface area carbon black from Cabot Corporation
20 were added to the solution, and the mix was sonicated for 1 hour at 40°C (preparation of the noble metal precursor solution further containing carbon particles).

8.64 g of $(\text{NH}_4)_2\text{S}_2\text{O}_3$ were diluted in 60 ml of deionised water, after which a pH of 7.64 was determined (preparation of the aqueous solution containing a
25 thionic species).

The rhodium/Vulcan solution was heated to 70°C while stirring and monitoring the pH. Once reached 70°C, the thiosulphate solution was added in four equivalent aliquots (15 ml each), one every 2 minutes. Between each addition, constancy of pH, temperature and colour of the solution were checked.

30 After the last aliquot of thiosulphate solution was added, the resulting solution was heated to 100°C and temperature was held for 1 hour. The reaction was monitored by checking the colour changes: the initial deep pink/orange colour,

which progressively changed to brown as the reaction progressed, finally turned to colourless upon completion of the reaction, thus indicating a total absorption of the products on the carbon. Spot tests were also carried out in this phase at various times with a lead acetate paper, which confirmed that no free sulphide ion was present in the reaction environment at any time. The precipitate was allowed to settle and then filtered; the filtrate was washed with 1000 ml deionised water to remove any excess reagent, then a filter cake was collected and air dried at 110°C overnight.

The dried product was finally subjected to heat treatment under flowing argon for 1 hour at 650°C, resulting in a weight loss of 22.15%.

The resulting carbon supported catalyst was first characterised in a corrosion test, to check its stability in a hydrochloric acid electrolysis environment.

For this purpose, part of the sample was heated to boiling in a chlorine-saturated HCl solution, at the same conditions disclosed in Example 4 of US 6,149,782. The colour of the resulting solution was the characteristic trace pink of the more stable forms of rhodium sulphide.

Actual performances in hydrochloric acid electrolysis of the catalyst prepared according to the method of the invention and incorporated in a gas-diffusion structure on a conductive web as known in the art were also checked. A catalyst/binder layer with a noble metal loading of 1 mg/cm² was obtained on an ELAT[®] carbon cloth-based gas diffuser produced by De Nora North America/USA; PTFE from an aqueous suspension was used as the binder. The gas diffusion-electrode thus obtained was sintered at 340°C under forced ventilation, and then used as an oxygen-reducing cathode in a hydrochloric acid electrolysis lab cell. A steady voltage consistently below 1.2 V at 4 kA/m² was recorded during a two week operation, which is an indication of an excellent electrochemical behaviour.

EXAMPLE 2

A rhodium sulphide catalyst equivalent to the one of the previous example was prepared in a similar way, the difference being that sodium tetrathionate was used as thionic species, instead of ammonium thiosulphate.

7.62 g of $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ were dissolved in 1 litre of deionised water, and the solution was refluxed (preparation of the noble metal precursor solution).

7 g of Vulcan XC72-R high surface area carbon black from Cabot Corporation were added to the solution, and the mix was sonicated for 1 hour at 40°C (preparation of the noble metal precursor solution further containing carbon particles).

17.86 g of $\text{Na}_2\text{S}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ were diluted in 100 ml of deionised water, after which a pH of 7.72 was determined (preparation of the aqueous solution containing a thionic species).

10 The rhodium/Vulcan solution was heated to 70°C while stirring and monitoring the pH. Once reached 70°C, the tetrathionate solution was added in four equivalent aliquots (25 ml each), one every 2 minutes. Between each addition, constancy of pH, temperature and colour of the solution were checked.

After the last aliquot of tetrathionate solution was added, the resulting solution was heated to boiling for 1 hour. The reaction was monitored by checking the colour changes: the initial yellow colour, which progressively changed to brown as the reaction progressed, finally turned to colourless upon completion of the reaction, thus indicating a total absorption of the products on the carbon. Spot tests were also carried out in this phase at various times with a lead acetate paper, which confirmed that no free sulphide ion was present in the reaction environment at any time. The precipitate was allowed to settle and then filtered; the filtrate was washed with 1000 ml deionised water to remove any excess reagent, then a filter cake was collected and air dried at 110°C overnight.

25 The dried product was finally subjected to heat treatment under flowing nitrogen for 2 hours at 650°C, resulting in a weight loss of 24.65%.

The resulting carbon supported catalyst was subjected to the same corrosion and electrochemical tests of the previous example, showing identical results.

Equivalent rhodium sulphide catalysts were obtained also by using sodium trithionate tetrathionate and heptathionate precursors previously prepared according to known procedures, with minor adjustments easily derivable by one skilled in the art. Analogous corrosion and electrochemical results were obtained also in these cases.

EXAMPLE 3

A rhodium-molybdenum sulphide catalyst was prepared by means of the following procedure: in a 500 ml, 250 ml of a previously refluxed 3g/l solution of
5 $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ were added (about 0.75 g of Rh, equivalent to 0.0073 moles). 3.37 g of Vulcan XC72-R high surface area carbon black from Cabot Corporation were added to the solution, and the mix was sonicated for 1 hour at 40°C (preparation of the noble metal precursor solution further containing carbon particles). 1.9 g of tetrathiomolybdate $(\text{NH}_4)_2\text{MoS}_4$ were diluted in 70 ml of
10 deionised water (preparation of a solution of a thionic species containing a second metal, in this case a non noble metal thionate).

The rhodium-Vulcan precursor solution was heated to 70°C while stirring and monitoring the pH. Once reached 70°C, the tetrathiomolybdate solution was added in four equivalent aliquots, one every 2 minutes. Between each addition,
15 constancy of pH, temperature and colour of the solution were checked.

After the last aliquot of tetrathiomolybdate solution was added, the resulting solution was heated to boiling for 1 hour. The reaction was monitored by checking the colour changes: the initial yellow colour, which progressively changed to light yellow as the reaction progressed, finally turned to colourless
20 upon completion of the reaction, thus indicating a total absorption of the products on the carbon. Spot tests were also carried out in this phase at various times with a lead acetate paper, which confirmed that no free sulphide ion was present in the reaction environment at any time. The precipitate was allowed to settle and then filtered; the filtrate was washed with 500 ml of warm (80°C)
25 deionised water to remove any excess reagent, then a filter cake was collected and air dried at 110°C overnight.

EXAMPLE 4

A ruthenium-rhodium sulphide catalyst was prepared by means of the following
30 procedure: in a 500 ml beaker, 100 ml of a previously refluxed 12 g/l solution of $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ (about 1.2 g of Ru^{+3}) and 100 ml of a previously refluxed 3 g/l

solution of $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ (about 0.75 g of Rh) were added, with a consequent weight ratio of about 80% Ru and 20% Rh.

The solution was brought to 350 ml with deionised water and 3.5 g of Vulcan XC72-R high surface area carbon black from Cabot Corporation were added.

- 5 The mix was sonicated for 1 hour at 40°C (preparation of the precursor solution of two distinct noble metals further containing carbon particles).

4.35 g of $(\text{NH}_4)_2\text{S}_2\text{O}_3$ were diluted in 20 ml of deionised water, after which a pH of 7.64 was determined (preparation of the aqueous solution containing a thionic species).

- 10 The rhodium-ruthenium/Vulcan solution was heated to 70°C while stirring and monitoring the pH. Once reached 70°C, the thiosulphate solution was added in four equivalent aliquots (5 ml each), one every 2 minutes. Between each addition, constancy of pH, temperature and colour of the solution were checked. After the last aliquot of thiosulphate solution was added, the resulting solution
- 15 was heated to 100°C and temperature was held for 1 hour. The reaction was monitored by checking the colour changes: the initial deep pink/orange colour, which progressively changed to brown as the reaction progressed, finally turned to colourless upon completion of the reaction, thus indicating a total absorption of the products on the carbon. Spot tests were also carried out in this phase at
- 20 various times with a lead acetate paper, which confirmed that no free sulphide ion was present in the reaction environment at any time. The precipitate was allowed to settle and then filtered; the filtrate was washed with 700 ml of warm deionised water to remove any excess reagent, then a filter cake was collected and air dried at 110°C overnight.

- 25 The above description shall not be understood as limiting the invention, which may be practised according to different embodiments without departing from the scopes thereof, and whose extent is solely defined by the appended claims.

- In the description and claims of the present application, the word "comprise" and its variations such as "comprising" and "comprises" are not intended to
- 30 exclude the presence of other elements or additional components.

CLAIMS

1. A noble metal sulphide catalyst obtained by reacting the precursor of at least one noble metal with a thionic species in an aqueous environment
5 essentially free of sulphide ions.
2. A carbon supported noble metal sulphide catalyst obtained by reacting the precursor of at least one noble metal with a thionic species in an aqueous environment essentially free of sulphide ions, containing suspended carbon particles.
- 10 3. The catalyst of claim 2 wherein said carbon particles are carbon black particles with surface area exceeding 50 m²/g.
4. The catalyst of anyone of claims 1 to 3 wherein the pH of said aqueous environment is comprised between 0.1 and 4.
5. The catalyst of anyone of claims 1 to 4 wherein said precursor of at
15 least one noble metal is a noble metal chloride.
6. The catalyst of anyone of claims 1 to 4 wherein said at least one noble metal is selected from the group consisting of ruthenium, rhodium, platinum, iridium and palladium.
7. The catalyst of anyone of claims 1 to 6 wherein said thionic species is
20 selected from the group of thiosulphates, dithionates, trithionates, tetrathionates, pentathionates, heptathionates and noble or non noble metal thionates.
8. The catalyst of claim 7 further subjected to a thermal treatment at a temperature comprised between 150 and 700°C.
- 25 9. A gas diffusion electrode comprising the catalyst of anyone of the preceding claims on a conductive web.
10. A method for producing a noble metal sulphide catalyst comprising reacting a solution of a precursor of at least one noble metal, optionally a chloride, with an aqueous solution containing a thionic species in an essentially
30 sulphide-free environment.

11. The method of claim 10 wherein the pH of said solution of a precursor of at least one noble metal and said aqueous solution containing a thionic species is comprised between 0.1 and 4 .
12. The method of claim 11 wherein said solution of a precursor of at least
5 one noble metal further contains carbon particles, optionally a carbon black with surface area exceeding 50 m²/g.
13. The method of anyone of claims 10 to 12 wherein said thionic species is selected from the group of thiosulphates, dithionates, trithionates, tetrathionates, pentathionates, heptathionates and noble or non noble metal
10 thionates, optionally as sodium or ammonium salts.
14. The method of claim 10 wherein said aqueous solution containing a thionic species is added to said solution of a precursor of a noble metal in discrete aliquots, optionally 2 to 10 equivalent aliquots at a time interval of 15 seconds to ten minutes.
15. The method of anyone of claims 10 to 14 wherein said aqueous
15 solution containing a thionic species is added to said solution of a precursor of at least one noble metal and the resulting solution is brought to boiling temperature from 5 to 120 minutes until completion of the reaction.
16. The method of claim 15 wherein said completion of the reaction is
20 determined by detection of a colour change.
17. The method of claim 15 further comprising isolating the resultant noble metal sulphide catalyst and subjecting the same to a thermal treatment at a temperature comprised between 150 and 700°C.
18. The method of anyone of claims 10 to 17 wherein said at least one
25 noble metal is selected from the group consisting of ruthenium, rhodium, platinum, iridium and palladium.