

## IMPROVEMENTS IN THE MANUFACTURE OF ELECTRODES

This invention relates to a method of forming an electrode material or an electrode coating by thermal decomposition of a liquid composition containing electrode component metal.

Electrodes are used on a commercial scale in various electrochemical processes such as electrolyses or electrolytic treatments, and in galvanic cells. Electrodes of various types and modes for various applications have been manufactured. These electrodes are preponderantly in the form of insoluble solids. Generally, metals or metal compounds, such as oxides thereof which possess the activity and durability expected of any electrode, are used either in the form of particles or deposited in the form of coatings on suitable substrates.

Insoluble electrodes formed by coating a substrate of metallic titanium with metal oxides including platinum group metal oxides, for example, are widely used on a commercial scale for electrolysis of aqueous solutions such as of sodium chloride. Electrodes formed of particles of metals or metal oxides and electrodes formed by sintering such particles or molding such particles with suitable binders have been used in electrolyses, electrolytic treatments and galvanic cells.

Electrodes of the types described above can be prepared by various methods. Among those methods,

there finds general acceptance as being highly effective the so-called thermal decomposition method which comprises the steps of preparing a liquid composition containing an electrode component metal and subjecting this liquid composition either directly, or after application to a substrate, to thermal decomposition, thereby converting the component metal into an electrode material in the form of a metal or a metal oxide.

Generally in this particular method, a composition containing a salt of a thermally decomposable electrode component metal and a solvent is subjected to thermal decomposition at an elevated temperature of about 250° to 800°C. Thermally decomposable salts which can be used include chlorides, oxychlorides, alkoxy halides, resins and amines, of various electrode component metals. As solvents therefor, water, hydrochloric acid, various alcohols, toluene, and benzene have been suitably adopted (as disclosed in Japanese Patent Publication SHO-48(1973)-3954 corresponding to U.S. Patent 3,711,385 and Japanese Patent Application Laid-Open SHO 51(1976)-131475, for example).

However, when a conventional composition for electrode production is subjected to a thermal treatment aimed at removing the solvent through volatilization and thermally decomposing the metal salt into a corresponding metal, or further converting the metal into a corresponding metal oxide, the electrode component metal is

often diffused in a large volume as volatilized in the form of a chloride in conjunction with the solvent. This results in serious problems including lowered product yield, impaired product quality stability and inevitable environmental pollution.

As a counter-measure, it has been proposed, where Sn is used as an electrode-coating component, for example, to use a sulfate of Sn instead of a chloride of Sn (as disclosed in Japanese Patent Application Laid-Open SHO 52(1977)-141489, for example). This method is effective in lowering the loss of the Sn component by volatilization to some, but not at present to a sufficient, extent. Furthermore, a danger arises from the use of sulfuric acid, a strong acid. With respect to component electrode materials other than Sn, the aforementioned problems remain unsolved. Thus, it has been difficult to produce electrodes formed of various electrode component materials in a stable manner and in high yields by the thermal decomposition method.

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According to the present invention we provide a method of manufacturing an electrolytic electrode comprising steps of:

a) forming a solution containing an electrode component metal selected from aluminium, tin, antimony, germanium, bismuth, gallium, indium, titanium, zirconium, tantalum, hafnium, vanadium, molybdenum, tungsten, ruthenium, palladium and iridium, and at least one organic compound selected from ascorbic acid, pyragallol, pyridinepenta-  
10 carboxylic acid, 8-hydroxyquinone-5-sulfonic acid and aluminon as a ligand capable of forming a complex with metal ions of said electrode component metal;

b) coating the solution thus formed onto an electrode substrate; and

15 c) subjecting said coated substrate to thermal treatment at an elevated temperature of from 250°C to 800°C in an oxidative atmosphere, wherein the volatilization and diffusion of said electrode component metal combined with said organic compound is prevented during the thermal  
20 treatment.

~~[This invention is applicable equally effectively to the manufacture of an electrode which does not involve use of a substrate and to the manufacture of an electrode deposited in the form of a coating on a substrate.]~~ The

5 substrate may be formed of any of the various electroconductive and durable materials and have any of the shapes heretofore used in anodes and cathodes. For example, valve metals such as Ti, Ta, Nb, and Zr are typical substrates for anodes and Fe and Ni, are typical  
10 substrates for cathodes.

Various electrode materials formed by thermal treatment can be produced to suit various applications. They possess electrochemical catalytic properties and durability and they generally have the form of metals,  
15 metal oxides, or mixtures thereof. To form such an electrode material in a free state or deposited on a substrate, a liquid composition containing a corresponding electrode component metal is prepared and subjected to thermal treatment while ~~held in a vessel~~  
20 ~~or~~ deposited on a suitable substrate. As already described, when a conventional composition is used and subjected to thermal treatment at an elevated temperature of from about 250° to 800°C, the electrode component metal is not entirely retained in the form of metal or  
25 metal oxide or deposited stably on the substrate but is readily volatilized into a chloride, for example, and

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diffused in large amounts into the ambient air possibly  
entailing difficulties such as lowered product yield and  
impaired stability of product quality. Among various  
electrode components metals, Al, Sn, Ge, Bi, Ga, In, Ti,  
5 Zr, Ta, Hf, V, Mo, Ru, Pd, Ir, etc. exhibit the afore-  
mentioned tendency conspicuously because the temperatures  
at which they are converted into their oxides are higher  
than the temperatures at which their chlorides are  
volatilized.

10 It has now been found that when, in accordance with  
the invention, the thermally-decomposable composition  
incorporates an organic compound capable of forming a  
complex with the metal ions, the difficulties described  
above are eliminated because the amount of electrode  
15 component metal which is readily volatilized and diffused  
during the thermal treatment is decreased to a notable  
extent.

The reason for this effect is not completely clear  
at present. Without desiring to be bound thereby, we  
20 postulate that the metal ions in the liquid composition  
are stabilised by the formation of a complex with the  
ligand, thus preventing volatilization and diffusion  
during the course of the thermal treatment and allowing  
the electrode materials, such as a metal or metal oxide,  
25 to be formed in high yield.

The organic compound, for use in this invention,  
must be capable of acting as a ligand and forming a

complex with a metal ion; the aforesaid five organic compounds meet this requirement. These compounds are capable of forming a complex with the electrode component metal in ordinary liquid compositions such as aqueous solutions or aqueous alcohol solutions, and they volatilize or decompose at a temperature below about 300°C and allow a metal or metal oxide to be produced from the metal ion combined therewith. From this point of view, the organic compound preferably has, in general, a small number (up to 12, for example) of carbon atoms because volatilization, decomposition and oxidation proceed quickly when the number of carbon atoms is small. An organic compound having a large number of carbon atoms, however, can be rendered effective for use by supplying an ample amount of oxygen to the reaction system, sufficient to ensure a thorough combustion of the organic compound.

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20 This invention is further illustrated by reference to the following non-limiting Examples. Unless otherwise indicated herein, all parts, percents, ratios and the like are by weight.

Example 1

25 A liquid composition was prepared by thoroughly mixing 10 ml of an aqueous solution of 0.5 g of chloroplatinic acid as Pt, 1.1 g of iridium chloride as Ir, and 0.5 g of titanium trichloride as Ti with

40 ml of an aqueous solution containing 1.7 g of stannous chloride as Sn, and 10 g of ascorbic acid.

In a crucible, the liquid composition was calcined at 550°C. to obtain a residue preponderantly in the metal oxide form. This residue was analyzed by a fluorescent X-ray method to determine the yields of component metals of the produced substance relative to the starting materials. The results obtained are shown in Table 1 below.

In a Comparative Example, a composition obtained by mixing 10 ml of an aqueous solution of 0.5 g of chloroplatinic acid as Pt, 1.1 g of iridium chloride as Ir, and 0.5 g of titanium trichloride as Ti with 30 ml of a 20% hydrochloric acid solution containing 1.7 g of stannous chloride as Sn and 10 ml of isopropyl alcohol was similarly calcined.

Table 1

Yield of Component Metal (%)

|                       | <u>Pt</u> | <u>Ir</u> | <u>Ti</u> | <u>Sn</u> |
|-----------------------|-----------|-----------|-----------|-----------|
| Example 1             | 99        | 98        | 96        | 98        |
| Comparative Example 1 | 98        | 74        | 71        | 59        |

Example 2

As a substrate, a commercially available pure titanium plate, 50 mm x 50 mm x 3 mm (thickness), was degreased with acetone and pickled with oxalic acid. The same liquid composition as described in Example 1 was coated on the substrate with a brush, dried at

room temperature (about 20-30°C), and heated at 550°C for 10 minutes in an electric oven with forced circulation of air therethrough. By performing the steps of application and calcining of the liquid composition for a total of 20 cycles, an electrode having a coating 3  $\mu$  in thickness was produced. In a Comparative Example, the same liquid composition as described in Comparative Example 1 was used similarly to produce an electrode.

The electrodes were analyzed by a fluorescent X-ray method to determine the ratio of electrode coating component metal retained on the substrate. The results obtained are shown in Table 2 below.

Table 2

Ratio of Component Metal Retained (%)

|                       | <u>Pt</u> | <u>Ir</u> | <u>Sn</u> |
|-----------------------|-----------|-----------|-----------|
| Example 2             | 99        | 99        | 98        |
| Comparative Example 2 | 99        | 71        | 45        |

(Note) The data on the Ti component are omitted because the determination of this component was difficult due to the influence of the Ti component in the substrate upon which the coating was placed.

It can be seen from the results of Example 1 and Example 2 that when ascorbic acid as a ligand capable of forming a complex with a metal ion was added in accordance with the method of this invention to the liquid composition, the electrodes were obtained in high yields and high retention ratios because

virtually no loss occurred in any of the electrode component metals as compared with the electrodes of Comparative Examples 1 and 2.

Example 3

5           A liquid composition was prepared by mixing 0.5 g of chloroplatinic acid as Pt, 0.55 g of iridium chloride as Ir, 1.5 g of aqueous tantalum pentachloride solution as Ta, 0.2 g of cobalt chloride as Co, and 0.55 g of stannic chloride as Sn with 20 ml of  
10       20% hydrochloric acid, 10 ml of butanol, and 5 g of pyrogallol.

          In a Comparative Example, a similar liquid composition was prepared using the procedure just described, except that the addition of pyrogallol was  
15       omitted.

          These liquid compositions were calcined in a crucible as in Example 1. The results obtained are shown in Table 3-1 below. They were also applied on a Ti substrate as in Example 2. The results obtained  
20       are shown in Table 3-2 below.

Table 3-1

Yield of Component Metal (%)

|                              | <u>Pt</u> | <u>Ir</u> | <u>Ta</u> | <u>Co</u> | <u>Sn</u> |
|------------------------------|-----------|-----------|-----------|-----------|-----------|
| Example 3-1                  | 99        | 99        | 97        | 99        | 98        |
| 25   Comparative Example 3-1 | 99        | 73        | 36        | 98        | 31        |

Table 3-2

Ratio of Component Metal Retained (%)

|                           | <u>Pt</u> | <u>Ir</u> | <u>Ta</u> | <u>Co</u> | <u>Sn</u> |
|---------------------------|-----------|-----------|-----------|-----------|-----------|
| Example 3-2               | 98        | 99        | 99        | 98        | 99        |
| 5 Comparative Example 3-2 | 98        | 62        | 23        | 98        | 25        |

Example 4

Three coating solutions were prepared by mixing 15 g of ruthenium chloride as Ru, 3 g of palladium chloride as Pd, 12 g of stannic chloride as Sn, and 2.5 g of antimony chloride severally with (1) 200 ml of isopropyl alcohol, 220 ml of pure water, and 90 g of pyridine pentacarboxylic acid (Example 4), (2) 400 ml of isopropyl alcohol and 20 ml of concentrated hydrochloric acid (36%) (Comparative Example 4-1), and (3) 400 ml of isopropyl alcohol and 20 ml of concentrated sulfuric acid (98%) (Comparative Example 4-2).

The liquid compositions described above were applied to substrates of Ti by following the procedure of Example 2, except that the calcining temperature was changed to 570°C to obtain electrodes. These electrodes were tested for retention ratios of component metals. The results obtained are shown in Table 4 below.

Table 4  
Ratio of Component Metal Retained (%)

|                           | <u>Ru</u> | <u>Pd</u> | <u>Sn</u> | <u>Sb</u> |
|---------------------------|-----------|-----------|-----------|-----------|
| Example 4                 | 97        | 99        | 99        | 98        |
| 5 Comparative Example 4-1 | 92        | 40        | 12        | 23        |
| Comparative Example 4-2   | 90        | 82        | 81        | 43        |

Example 5

10 A liquid coating composition was prepared by adding 40 g of 8-hydroxyquinone-5-sulfonic acid to an aqueous hydrochloric acid solution (5%) containing 1.40 g of chloroplatinic acid as Pt, 0.45 g of palladium chloride as Pd, 9.5 g of stannic chloride as Sn, and 0.85 g of bismuth chloride as Bi and diluting the resultant solution with pure water to about 100 ml.

15 The coating composition so obtained was applied on the same type of titanium plate as in Example 2 with a brush, dried at 120°C for 5 minutes, and calcined at 500°C for 20 minutes. This procedure was performed for a total of 20 cycles to produce an electrode.

20 The coating composition and the electrode obtained by applying this composition on the Ti substrate were analyzed to determine the percentage composition of electrode component metals. The results obtained are shown in Table 5 below.

Table 5

Composition of Component Metals (mol%)

|                       | <u>Pt</u> | <u>Pd</u> | <u>Sn</u> | <u>Bi</u> |
|-----------------------|-----------|-----------|-----------|-----------|
| Liquid Composition    | 7.53      | 4.46      | 83.7      | 4.27      |
| 5 Electrode Deposited | 7.74      | 4.37      | 80.4      | 4.36      |

It can be seen from the results in Table 5 that, if produced by the method of this invention, the electrode deposited on the substrate had substantially the same composition of component metal as the coating composition, indicating that the electrode deposited on the substrate retained the component metals at high retention ratios because virtually no volatilization occurred during the course of heating and calcining.

Example 6

15 A liquid coating composition was prepared by adding 50 g of aluminon to 5.15 g of rhodium chloride as Rh, 2.53 g of ruthenium chloride as Ru, 2.5 g of antimony chloride as Sb, 1.5 g of aqueous hydrochloric acid solution (20%) of tantalum pentachloride as Ta, 20 and 3.5 g of aqueous hydrochloric acid solution (20%) of zirconium chloride as Zr and diluting the resultant solution with pure water to about 100 ml. From this coating composition, an electrode was produced by following the procedure of Example 5.

25 The coating composition and the electrode deposited on the substrate were analyzed to determine the

percentage composition of component metals. The results obtained are shown in Table 6 below.

Table 6

Composition of Component Metals (mol%)

| 5 |                     | <u>Rh</u> | <u>Ru</u> | <u>Sb</u> | <u>Ta</u> | <u>Zr</u> |
|---|---------------------|-----------|-----------|-----------|-----------|-----------|
|   | Liquid Composition  | 27.2      | 13.6      | 11.1      | 27.2      | 20.9      |
|   | Electrode Deposited | 27.4      | 14.2      | 10.7      | 26.9      | 20.8      |

As described above, the method of this invention enables an electrode to be manufactured in a high yield and high retention ratios of the component metals by preventing the possible loss of the component metals by vaporization during the course of heat treatment. It also permits an electrode of the required composition to be manufactured in a stable manner and with high repeatability. Thus, an electrode of high quality can be manufactured with ease by employing the method of the present invention.



CLAIMS:

1. A method of manufacturing an electrolytic electrode comprising the steps of:

a) forming a solution containing an electrode component metal selected from aluminium, tin, antimony, germanium, bismuth, gallium, indium, titanium, zirconium, tantalum, hafnium, vanadium, molybdenum, tungsten, ruthenium, palladium and iridium, and at least one organic compound selected from ascorbic acid, pyragallol, pyridinepentacarboxylic acid, 8-hydroxyquinone-5-sulfonic acid and aluminon as a ligand capable of forming a complex with metal ions of said electrode component metal;

b) coating the solution thus formed onto an electrode substrate; and

c) subjecting said coated substrate to thermal treatment at an elevated temperature of from 250°C to 800°C in an oxidative atmosphere, wherein the volatilization and diffusion of said electrode component metal combined with said organic compound is prevented during the thermal treatment.

2. A method as claimed in Claim 1 and substantially as hereinbefore described.

3. A method of forming an electrode material or an electrode coating, substantially as hereinbefore described with reference to any one of Examples 1 to 6.

4. An electrode formed of, or coated with, a material formed by a method as claimed in any preceding claim.