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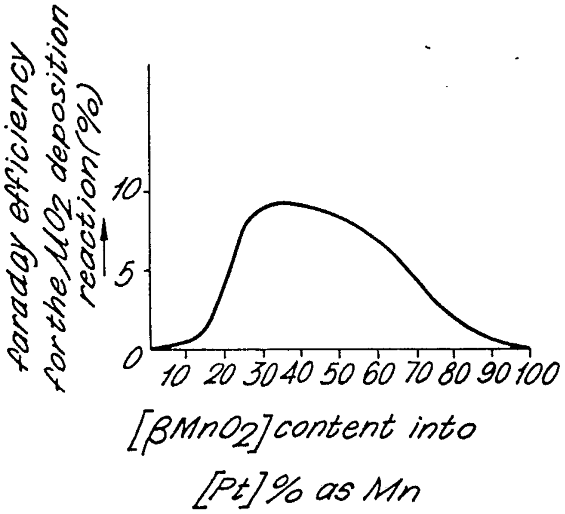
(54) Title: ELECTRODES FOR ELECTROLYTIC PROCESSES, ESPECIALLY METAL ELECTROWINNING

(57) Abstract

An electrode for electrolytic processes such as the recovery of uranium dioxide from seawater comprises an electrically-conductive corrosion-resistant substrate having an electrocatalytic coating which is preferably a mixture of 30 to 80 parts by weight of platinum, 20 to 70 parts by weight (as Mn metal) of ß-MnO2 and 2 to 10 parts by weight (as Sn metal) of tin dioxide.



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ELECTRODES FOR ELECTROLYTIC PROCESSES, ESPECIALLY METAL ELECTROWINNING

TECHNICAL FIELD

The invention relates to electrodes for electrolytic processes, in particular to electrodes having an active surface containing manganese dioxide, and to electrolytic processes using such electrodes, especially as anodes for metal electrowinning.

BACKGROUND ART

Anodes made of manganese oxides have been known for a long time and are disclosed, for instance, in U.S. Patent Specifications 1,296,188 and 1,143,828. Such anodes have been used in the electrowinning of metals such as zinc, copper and nickel. For various reasons, such as the difficulties met with in forming them, such anodes are not suitable for commercial use, however. Another proposed electrode is described in U.S. Patent Specification 3,855,084, wherein titanium particles are cemented together with thermally-deposited manganese dioxide and a second or outer coating of electrodeposited manganese dioxide is provided thereon.

U.S. Patent Specification 3,616,302 describes an electrowinning anode, comprising a sandblasted titanium substrate coated with a thin intermediate layer of platinum, palladium or rhodium or their alloys, on which a relatively thick layer of manganese dioxide is electroplated.

U.S. Patent Specification 4,028,215 discloses an electrode which comprises a valve metal substrate, an intermediate semi-conductive layer of tin and antimony oxides and a top coating of manganese dioxide.

More recently, U.S. Patent Specification 4,077,586 proposed an electrode having a corrosion-resistant substrate coated with β-manganese dioxide, chemideposited by thermal decomposition of an alcoholic solution of manganese nitrate, and activated by β-ray irradiation or by the addition of up to 5% by weight of at least one metal from groups IB, IIB, IVA, VA, VB, VIB, VIIB and VIII of the Periodic Table, excluding the platinum group metals, gold and silver. The corrosion-resistant substrate was optionally provided with a thin porous intermediate coating, such as a valve metal or a platinum group metal or oxide thereof, and the activated manganese dioxide optionally contained up to 20% by weight of silicon dioxide, β-lead dioxide or tin dioxide as stabilizer.

DISCLOSURE OF INVENTION

An object of the invention is to provide an improved electrode, having a coating of manganese dioxide which selectively favours oxygen evolution, the electrode being particularly useful for electrowinning metals from dilute solutions.

According to a main aspect of the invention, an electrode for electrolytic processes comprises an electrically-conductive corrosion-resistant substrate having an electrocatalytic coating, characterized in that the coating contains a mixture of at least one platinum group metal and manganese dioxide dispersed in one another throughout the coating, in a ratio of from 8:2 to 3:7 by weight, of the platinum group metal(s) to the manganese metal of the manganese dioxide. Preferably, the coating contains platinum in a ratio of from 7:3 to 4:6 by weight.

The platinum-group metal/manganese dioxide coating preferably also contains, as a stabilizer, titanium oxide, silicon dioxide, β-lead dioxide and/or tin dioxide, most preferably tin dioxide. The presence of a stabilizer is especially useful when the manganese content exceeds the platinum group metal content, in order to prevent corrosion of the coating during electrolysis. Additionally, the coating may include a filler, e.g. particles or fibres of an inert material such as silica or alumina, particles of titanium or, advantageously, zirconium silicate. Furthermore, depending on the use to which the electrode is to be put, the mixed coating of platinum group metal(s) and manganese dioxide may also contain, as dopant, up to about 5% by weight as metal of the manganese dioxide, at least one additional metal selected from groups IB, IIB, IVA, VA, VB, VIB and VIIB of the periodic table and iron, cobalt and nickel. Usually such stabilizers, fillers and dopants do not account for more than 70% of the total weight of the coating, usually far less. In the case of tin dioxide, the preferred amount is about 5% to 10% by weight of tin to the total weight of the platinum group metal(s) plus the manganese metal of the manganese dioxide.

The platinum group metals are ruthenium, rhodium, palladium, osmium, iridium and platinum. Platinum metal is preferred and is mentioned hereafter by way of example. However, it is to be understood that alloys such as platinum-rhodium and platinum-palladium can also be used. Also, in some instances, it may be advantageous to alloy the platinum group metal(s) with one or more non-platinum group metals, for example an alloy or an intermetallic compound with one of the valve metals, i.e. titanium, zirconium, hafnium, vanadium, niobium and tantalum, or with another transition metal, for example a metal such as tungsten, manganese or cobalt.

The substrate may consist of any of the aforementioned valve metals or alloys thereof, porous sintered titanium being preferred. However, other electrically-conductive and corrosion-resistant substrates may be used, such as expanded graphite.

The platinum group metal(s) and manganese dioxide with possible additional components, such as tin dioxide, may be co-deposited chemically from solutions of appropriate salts which are painted, sprayed or otherwise applied on the substrate and then subjected to heat treatment, this process being repeated until a sufficiently thick layer has been built up.

Alternatively, thin layers of different components (e.g. alternate platinum layers and layers of mixed β-manganese dioxide and tin dioxide) can be built up in such a way that the components are effectively mixed and dispersed in one another throughout the coating, possibly with diffusion between the layers, in contrast to the cited prior art coatings in which the manganese dioxide was applied as a separate top layer.

In all instances, the manganese dioxide is preferably in the β form, being chemi-deposited by thermal decomposition of a solution of manganese nitrate.

The platinum-group metal/manganese dioxide layer may be applied directly to the substrate or to an intermediate layer, e.g. of co-deposited tin and antimony oxides or tin and bismuth oxides or to intermediate layers consisting of one or more platinum group metals or their oxides, mixtures or mixed crystals of platinum group metals and valve metal oxides, intermetallics of platinum group metals and non-platinum group metals, and so forth.

In a preferred embodiment, the coating comprises 30 to 80 parts by weight of platinum, 20 to 70 parts by weight (as Mn metal) of β-manganese dioxide and 2 to 10 parts by weight (as Sn metal) of tin dioxide. This embodiment of an electrode of the invention, when used as anode for metalwinning from dilute solutions, has been found to have selective properties favouring oxygen evolution and the deposition of certain metal oxides, e.g. the anodic deposition of UO_2 from seawater. The platinum metal plays three roles: as an electronic conductor; as oxygen evolution catalyst (the wanted reaction); and as chlorine evolution poison (the unwanted reaction). Not only is β-manganese dioxide isomorphous with UO_2, but also it acts as a catalyst for UO_2 deposition. Finally, the tin dioxide, in addition to stabilizing the β-manganese dioxide, acts as a source of active oxygen (H_2O_2).

Another aspect of the invention is a method of electro-recovering metals, especially strategic metals such as uranium, yttrium and ytterbium, or their oxides, e.g. from dilute saline waters such as seawater, which comprises using as anode an electrode according to the invention, as defined above. This method is preferably carried out with deposition of the metal oxide in oxygen-evolving conditions.

BRIEF DESCRIPTION OF DRAWINGS

In the accompanying drawings:

Fig. 1 is a graph showing faraday efficiency of UO_2 deposition as ordinate plotted against the β-MnO_2 content by weight of Mn to the total weight of Mn + Pt group metal as abscissa, obtained by use of the electrode described in detail in Example I below;

Fig. 2 is a graph showing anode potential as ordinate plotted against current density as abscissa, obtained using the electrodes described in detail in Example III below.

BEST MODES FOR CARRYING OUT THE INVENTION

The following Examples are given to illustrate the invention:

Example I

Mixed coatings of platinum metal and $\beta\text{-}MnO_2$ were applied to expanded graphite anode bases by chemi-deposition from a solution containing platinum and manganese nitrates in isopropyl alcohol. After each application of the coating solution by brush, the anode bases were heated at 300° to $320^\circ C$ in an oven with air circulation, for about 10 minutes, and the procedure was repeated ten times for each anode base. The coated electrodes were then used for the recovery of UO_2 from a dilute saline solution containing 30g/l NaCl and 100 ppm of uranium acetate. The electrolyte was held at $20^\circ C$ and was stirred by ultrasounds. The faraday efficiency of the UO_2 deposition reaction was measured. Fig. 1 shows a graph of this faraday efficiency as a function of the $\beta\text{-}MnO_2$ content by weight of manganese metal to the total weight of manganese plus platinum metals in the coating. From this graph, it can be seen that there is an optimum value of the $\beta\text{-}MnO_2$ content of about 30% to 40% (as Mn metal) corresponding to the maximum UO_2 faraday efficiency. For Mn metal contents above 40%, corrosion and dissolution of the $\beta\text{-}MnO_2$ were observed, being detected by atomic adsorption analyses on the used electrolyte.

Example II

Expanded graphite anode bases were coated as in Example I, except that the coating solution additionally contained tin nitrate. The finished coatings contained

β-MnO_2 (50% by weight as Mn metal), Pt (40%-50% by weight as metal) and SnO_2 (0%-10% by weight as Sn metal). These anodes were used, under the same conditions as Example I, for UO_2 recovery. An optimum faraday efficiency for UO_2 deposition was achieved with an Sn content of from about 3% to 6%. No corrosion or dissolution of the MnO_2 was observed.

Example III

Examples I and II were repeated using porous sintered titanium anode bases which, prior to coating, were subjected to sandblasting with steel grit followed by etching in boiling HCl for about 10 minutes. These anodes gave similar results for UO_2 deposition under the same conditions as Examples I and II. Fig. 2 is a potentiostatic curve of such a sintered titanium anode coated with a chemi-deposited coating containing 45% by weight Pt, 50% by weight β-MnO_2 (as Mn metal) and 5% by weight SnO_2 (as Sn metal). The corresponding curve for a platinum-coated sintered titanium anode is shown as a dashed line. No UO_2 deposition was obtained on the platinum-coated anode, which gave simultaneous chlorine and oxygen evolution at mixed potential. For the Pt-β-MnO_2-SnO_2 coated anode, UO_2 deposition started at a potential of about 1.0 V(NHE), while oxygen evolution took place at 1.4V (NHE) and chlorine evolution at 1.7 V(NHE). Under chlorine evolving conditions, the deposited UO_2 was found to dissolve rapidly, while no dissolution of the UO_2 deposit took place under oxygen evolving conditions. Further, the UO_2 deposition rate was observed to be greater at the oxygen evolution potential than at lower potential. This graph may be explained by the following reactions:

(i) direct electrochemical oxidation of low valent uranium species, e.g.

$$U^{III}O^{+} + H_2O \longrightarrow \left[U^{IV}O_2\right]\downarrow \quad + 2H^{+} + e$$

(ii) catalytic chemical oxidation of low valent uranium species by atomic oxidation or peroxide compounds:

$$H_2O \longrightarrow \underset{\substack{\text{active}\\ \text{oxygen}}}{O} + 2H^{+} + 2e$$

$$\underset{\substack{\text{active}\\ \text{oxygen}}}{2O} + U^{III} \longrightarrow \left[UO_2\right]\downarrow$$

Reaction (ii) is favoured by the presence of SnO_2, which acts as a source of active oxygen by complexing H_2O_2 in addition to stabilizing the MnO_2 phase.

CLAIMS

1. An electrode for electrolytic processes, comprising an electrically-conductive corrosion-resistant substrate having an electrocatalytic coating, characterized in that the coating contains a mixture of at least one platinum group metal and manganese dioxide dispersed in one another throughout the coating in a ratio of from 8:2 to 3:7 by weight of the platinum group metal(s) to the manganese metal of the manganese dioxide.

2. The electrode of claim 1, characterized in that the coating contains platinum in a ratio of 7:3 to 4:6 by weight of the platinum to the manganese metal of the manganese dioxide.

3. The electrode of claim 1 or 2, characterized in that the coating further contains silicon dioxide, β-lead dioxide and/or tin dioxide as stabilizer.

4. The electrode of claim 1, characterised in that the coating contains 30 to 80 parts by weight of platinum, 20 to 70 parts by weight (as Mn metal) of β-manganese dioxide and 2 to 10 parts by weight (as Sn metal) of tin dioxide.

5. The electrode of any preceding claim, characterized in that the electrocatalytic coating containing the platinum group metal(s) and manganese dioxide is applied to an intermediate conductive layer carried on the substrate.

6. A method of recovering metals or their oxides by electrolysis, characterized by using as anode the electrode as claimed in any one of

claims 1 to 5.

7. A method of recovering metals or their oxides by electrolysis using an anode comprising an electrically-conductive corrosion-resistant substrate having an electrocatalytic coating,
characterized by
using an anode having at least one platinum group metal and manganese dioxide dispersed in one another throughout its electrocatalytic coating.

8. The method of claim 6 or 7, wherein uranium dioxide is recovered from a dilute saline electrolyte such as seawater.

Fig. 1.

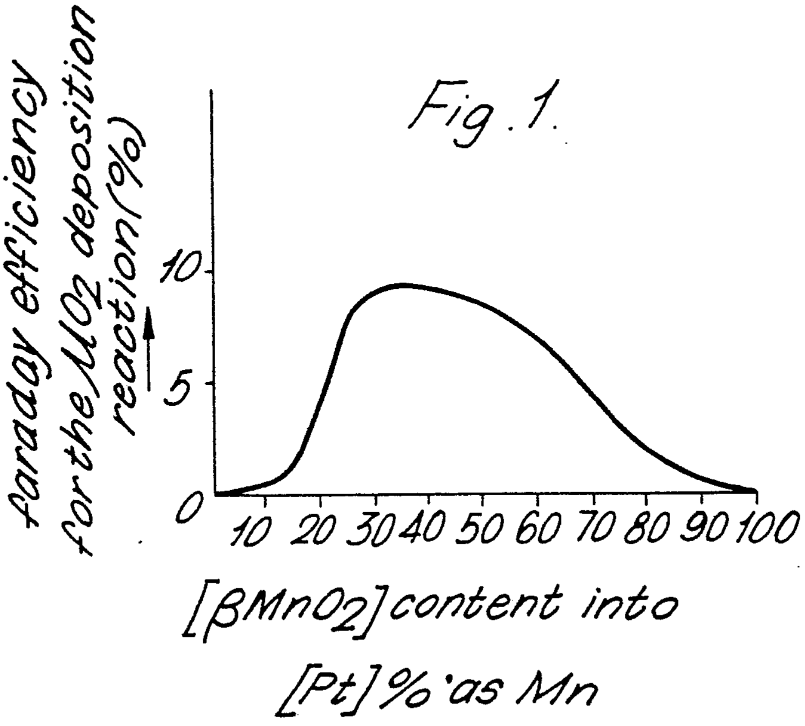
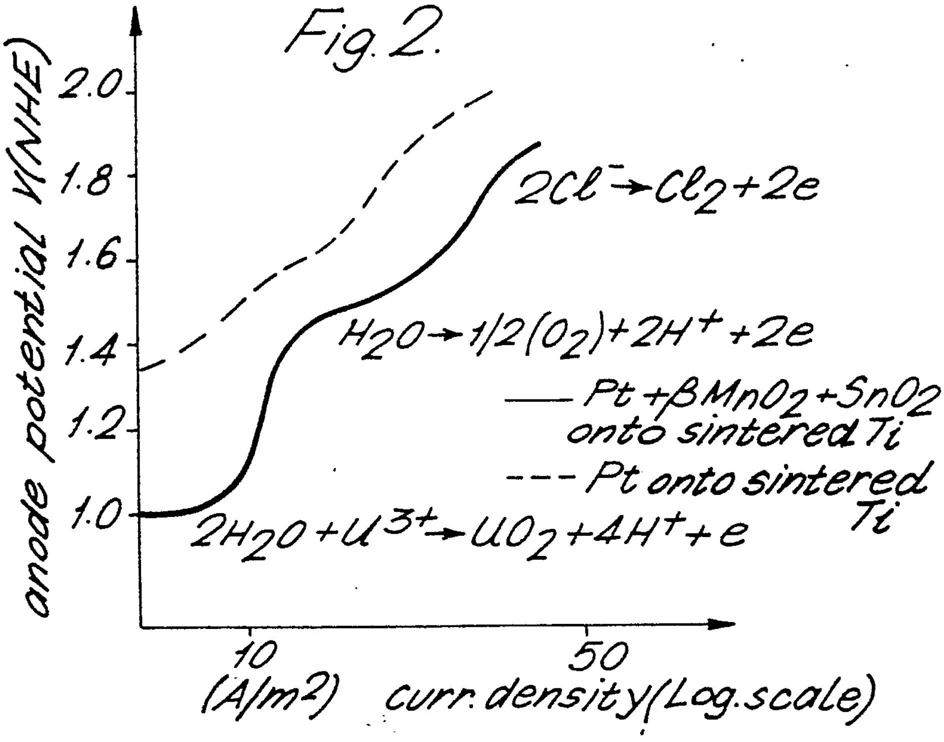

faraday efficiency for the UO2 deposition reaction (%)
0
5
10
10
20
30
40
50
60
70
80
90
100
[βMnO2] content into [Pt] % as Mn

Fig. 2.


anode potential V(NHE)
1.0
1.2
1.4
1.6
1.8
2.0
10
50
(A/m2) curr. density (Log. scale)
2Cl⁻ → Cl2 + 2e
H2O → 1/2(O2) + 2H⁺ + 2e
2H2O + U³⁺ → UO2 + 4H⁺ + e
— Pt + βMnO2 + SnO2 onto sintered Ti
--- Pt onto sintered Ti

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 79/00020

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

C 25 B 11/06; C 25 C 7/02

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
Int.Cl.^{2}	C 25 B 11/06; C 25 C 7/02

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
	DE, A, 2652152, published September 15, 1977 see page 25, example A 2; page 4, claim 18, Diamond Shamrock Technologies	1
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* Special categories of cited documents: [15]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] 3rd July 1979	Date of Mailing of this International Search Report [2] 12th July 1979
International Searching Authority [1] European Patent Office	Signature of Authorized Officer [20] G.L.M.KRUYDENBERG

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