

1

3,574,074

**SURFACE TREATED PLATINIZED ANODES**  
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**ABSTRACT OF THE DISCLOSURE**

Power costs in the electrolytic production of chlorine using platinum metal surfaced anodes are reduced by first subjecting the anodes as electrodes to the action of alternating current in an electrolytic solution.

This invention relates to a process for activating platinum metal surfaces to enhance their use as anodes in the electrolysis of aqueous chloride brines for the production of chlorine. More particularly, according to the invention, the platinum surfaced anodes are used as electrodes in an electrolytic solution subjected to alternating current. The treated electrodes exhibit reduced chlorine overvoltage when used as anodes in direct current electrolysis of aqueous chloride brines and the voltage requirement for electrolysis is significantly reduced to effect a saving in power costs in the production of chlorine.

In the electrolytic production of chlorine using cells of the diaphragm or mercury cathode type, anodes having platinum metal surfaces are particularly advantageous for their complete resistance to the action of hot, wet chlorine gas. Anodes of pure platinum metal are suitable for this use and for treatment according to this invention but their use is usually considered prohibited by their cost. More recently, titanium anodes having a thin coating of a platinum metal have become widely used in chlorine-producing cells. They are equally inert chemically, light in weight and are economically competitive with the more commonly used graphite anodes, considering their relatively long life. These platinum metal coated titanium anodes are also suitably treated according to the process of this invention.

The art is aware of satisfactory methods for producing good, adhesive deposits of platinum, other platinum metals or their alloys on titanium. The platinum metal deposits on titanium are suitably produced by chemical, electrochemical, metal cladding, vapor deposition or by vacuum metallizing means. The process of this invention is equally useful for all types of such surfaces but preferably is applied to deposits which are well bonded to the substrate. The process of this invention is also useful for similar surfaces which have already been used in electrolysis but have lost their activity due to deposition of poisons or corrosion of their active sites, as long as a film of platinum metal is still present. Poisoning of platinum surfaces occurs due to partial loss of platinum metal from plated surfaces and also when platinum metal plated anodes are used in electrolysis of alkaline brine solutions.

One disadvantage of platinum metal surfaced anodes in the electrolysis of chloride brines is the high overvoltage of chlorine on such surfaces. As much as 500 millivolts (0.5 volt) or more may be required to effect the discharge of chlorine as gas. Added to other potential requirements in various parts of the cell, the total cell voltage may exceed 5 volts raising the power costs and the production cost of the chlorine. Since the chlorine overvoltage may amount to 10% of the total cell voltage, any significant reduction in the chlorine overvoltage materially reduces the production cost of chlorine. The process of the present invention generally reduces the chlorine overvoltage on the platinum metal surfaces to below 100 millivolts, gen-

2

erally in the range of about 40 to 80 millivolts and, under preferred conditions of operation to as low as about 25 millivolts.

The process of the present invention in general comprises activating a platinum metal surface for use as an anode in the electrolysis of aqueous chloride brines by subjecting the platinum surface as an electrode to the action of alternating current of 30 to 80 hertz at a temperature of from 20° to 100° C. in a chloride-free aqueous electrolyte.

By the term "platinum metal" in the present specification and claims is meant an element of the group consisting of ruthenium, rhodium, palladium, osmium, iridium and platinum or alloys of two or more of these metals. The term "titanium" is meant to include alloys consisting essentially of titanium.

Suitable aqueous electrolytes for use in the process of this invention are substantially free of chloride or other halide ions but generally other inorganic electrolytes are suitable. Examples include aqueous solutions of sulfuric acid, phosphoric acid, perchloric acid, sodium hydroxide, potassium chromate, potassium permanganate. Mixtures of phosphoric and sulfuric acids are suitable, for example, a mixture of 80 ml. of 98% H<sub>2</sub>SO<sub>4</sub>, 370 ml. of 85% phosphoric acid and 50 ml. of water gave excellent results. Organic electrolytes, for example, oxalic and acetic acids are also suitable. Concentrations are not critical and suitably vary over a wide range.

The frequency of the AC current is suitably in the range of 25 to 80 hertz. It is less effective at 100 hertz and at higher frequencies. Preferably the frequency is from about 25 to 60 hertz. The latter is conveniently available but lower frequencies result in lower chlorine overvoltage at the cost of slight losses of platinum.

The temperature of the AC treatment is not critical in the range from room temperature, say, 20° C., to 100° C.

Suitable current density in the AC treatment is from 0.5 to 6 amperes per square inch of platinum surface being treated. The current density should be maintained below the point at which gases are discharged on the electrode surface. At higher current densities, the treatment is less effective.

In the AC treatment a uniform black coating forms on the platinum surface in about 5 to 15 minutes at room temperature up to the boiling point of the aqueous electrolyte and the activation is complete. Additional time results in no further improvement in reducing the chlorine overvoltage.

In the AC electrolytic treatment, both electrodes are suitably platinum surfaced and both are subject to the same activation simultaneously whether they are anode or cathode. Alternatively the counter-electrode can be composed of any inert conductive material.

The electrode to be treated is first cleaned by any suitable procedure. Appropriately it is thoroughly degreased by washing with an organic solvent, for example, acetone or carbon tetrachloride or by boiling with aqueous sodium hydroxide. It is then washed to remove the degreasing agent, dipped in concentrated hydrochloric acid to remove metal impurities from the surface and rinsed again. It is then ready for treatment by the process of this invention.

The process of the present invention is useful for either a poisoned or inactive surface or a freshly plated surface. The process appreciably increases the activity of the electrode surface and also its resistance to chemical attack by brine or sodium amalgam.

In the following examples, overvoltage was measured by the current interrupter method. First a reference potential line was obtained as follows:

The test anode was first conditioned by electrolysis at 5 amperes per square inch at 70° C. in brine solution containing 260 to 300 grams per litre of sodium chloride for

20 to 30 minutes. A flow of 5 ml./min. of brine was maintained. An H-type diaphragm cell was used with platinum sheet or platinized titanium as cathode. A saturated calomel electrode with a Luggin capillary was the reference electrode.

After conditioning, the anode was polarized for 30 seconds at 5 amperes per square inch and the current was switched off using Clare model HGP-1004 mercury wetted relay switch. After 30 seconds, a trace was obtained and photographed from the reticule of a Hewlett-Packard model 130C oscilloscope. The time base (horizontal axis) for this trace was 5 microseconds/cm. and vertical axis was 0.1 or 0.2 volt/cm. depending upon the sensitivity required. This trace was the reference potential, i.e. the potential of a reversible chlorine anode.

Chlorine overvoltage was measured by polarizing the chlorine anode at a current density of 5 amperes per square inch at 70° C. for 30 seconds. The current was then interrupted and a decay of polarization curve at 5 microseconds/cm. time base was photographed from the reticule of a Hewlett-Packard model 130C oscilloscope. The overvoltage is the difference between the potential of the decay curve at equilibrium and the potential at the start of the decay curve.

#### EXAMPLE I

A number of platinum coated titanium electrodes used for various purposes and which had a high overvoltage of chlorine, were electrolyzed in 5% aqueous sulfuric acid for 5 to 15 minutes with 60 hertz (cycles) alternating current at a current density of 5 amperes per square inch at 5 volts. In every instance, the chlorine overvoltage measured at a current density of 5 amperes per square inch and 70° C. was materially reduced as shown in Table I.

TABLE I.—EFFECT OF AC TREATMENT ON OVERVOLTAGE

Anode No.	Chlorine overvoltage, mv:	
	Before treatment	After treatment
28.....	510	50
40.....	200	50
34.....	150	70
49.....	560	70
53.....	520	60
59.....	510	40
66.....	490	40
88.....	310	40
38.....	160	60

#### EXAMPLE II

Three of a number of platinum coated titanium electrodes which had a chlorine overvoltage of about 120 mv. measured at a current density of 5 amperes per square inch and at 70° C. were activated as described in Example I. Both the treated and the remaining untreated electrodes were intentionally poisoned by using them as anodes in electrolyzing concentrated alkaline sodium chloride brine having a pH of 10 to 12 and containing 260 to 300 grams per liter of NaCl at 5 amperes per square inch at 14 volts for about 5 hours. The chlorine overvoltage was measured at 5 amperes per square inch at 70° C. before and after the poisoning test. The results presented in Table II show that the poisoning treatment had little effect on the overvoltage displayed by the AC treated anodes. In contrast, the overvoltage shown by the untreated anodes after poisoning increased to about 500 mv.

TABLE II.—EFFECT OF POISONING OF AC TREATED SURFACES

Anode No.	Chlorine overvoltage, mv.	
	After AC treatment	After poisoning
38.....	60	90
66.....	40	60
88.....	40	60
.....	.....	500

#### EXAMPLE III

Evaluation of corrosion resistance test for the anode samples consisting in polarizing the anode at 5 a./in.<sup>2</sup>

current density in brine, switching off the polarizing current and observing the polarization decay curve and the time it took to decay to the reference potential after switching off the current. The samples that took longer time to decay to the reference potential were found to lose more weight in our laboratory tests. With this corrosion resistance test it was observed that the treated samples showed a polarization decay to reference potential in 100 milliseconds or less while the freshly prepared untreated samples took 20 to 30 seconds. This showed the greater resistance to corrosion of the AC treated samples.

Resistance to corrosion was also measured by dropping 0.2% sodium amalgam on the anode sample, wetting it with water and noting the amalgamation of the electrode surface. With the untreated surfaces, the amalgamation was almost instantaneous while the AC treated surfaces resisted amalgamation to a greater extent and in some cases were completely resistant to amalgamation.

#### EXAMPLE IV

Several platinum coated electrodes which had chlorine overvoltages of about 120 mv. were activated as described in Example I using 10% H<sub>2</sub>SO<sub>4</sub> as electrolyte and AC current at various frequencies. The chlorine overvoltages at 5 amperes per square inch were measured at 70° C. after activation. The results, presented in Table III, show that the activation treatment was effective at lower frequencies but at 100 hertz (and higher) the treatment was ineffective. At frequencies below 50 hertz some loss of platinum occurs. However, the surface shows extremely low chlorine overvoltage and is more resistant to corrosion and poisoning. The superior surface is economically advantageous compared to the cost of the small amount of platinum removed by low frequency AC treatment.

TABLE III.—EFFECT OF FREQUENCY OF AC TREATMENT

Anode No.:	Frequency, hertz	Chlorine overvoltage, mv.	Decay time, milliseconds
41.....	100	210	.....
45.....	80	80	.....
31.....	60	50	.....
44.....	50	35	5
42.....	40	25	1
40.....	30	25	0.02

#### EXAMPLE V

Two test anodes were installed in an E-8 cell such as described in Ind. Eng. Chem. 45, 1824-35 (1953) and the cell was operated for a period of about 15 months. The test anodes were strut-reinforced titanium sheets plated with platinum and one was additionally treated by electrolyzing in 5% aqueous sulfuric acid for 7 minutes at 3 to 5 volts using 60 hertz AC current of 800 amperes.

Brine cell tests were run at about 4.3 volts and current density was about 4.5 amperes per square inch of anode surface until performance indicated that the platinum surfaces had corroded away. Total life was used as a basis for calculating the cost of platinum per ton of chlorine. The data are presented in Table IV and show a power saving of \$1.15 per ton of chlorine resulting from use of the AC treatment of this invention compared to the untreated anode. The net cost shows a reduction of \$0.84 per ton of chlorine including the cost of the platinum, the cost of the AC treatment and the power saving. This is a material reduction in the production cost of chlorine at this stage in the form of wet cell gas, prior to purification and liquefaction.

TABLE IV

Treatment	Costs in dollars per ton of chlorine		
	Platinum	Power	Net
No AC treatment.....	2.89	0	2.89
AC treatment, 7 minutes.....	3.20	-1.15	2.05

**5**  
**EXAMPLE VI**

Platinum coated titanium electrodes showing high chlorine overvoltage were electrolyzed for 5 to 15 minutes in a solution of 50 ml. of water, 370 ml. of 85% phosphoric acid and 80 ml. of 98% sulfuric acid using 60 hertz AC current at a current density of 5 amperes per square inch at 5 volts. The chlorine overvoltage in each case was materially reduced as shown in Table V. In addition, each electrode was then subjected to the poisoning treatment described in Example II. The chlorine overvoltage of each electrode was again measured. The data in Table V show excellent resistance to the poisoning treatment.

TABLE V.—AC TREATMENT IN  $H_3PO_4-H_2SO_4$

Anode No.:	Chlorine overvoltage, mv.		
	Before treatment	After treatment	After poisoning
1.....	380	50	60
3.....	270	50	40
4.....	210	50	40
6.....	210	40	80
9.....	260	50	45

**EXAMPLE VII**

Platinum coated titanium electrodes were AC treated as described in Example VI, substituting 5% aqueous sodium hydroxide as the electrolyte. The chlorine overvoltage was reduced as shown in Table VI.

TABLE VI.—AC TREATMENT IN AQUEOUS CAUSTIC

Anode No.	Chlorine overvoltage, mv.	
	Before	After
52.....	140	40
62.....	190	40

**6**  
**EXAMPLE VIII**

A sheet of platinum showing a chlorine overvoltage of 430 millivolts was subjected to the AC treatment in  $H_3PO_4-H_2SO_4$  as described in Example VI. The chlorine overvoltage after treatment was reduced to 40 millivolts.

What is claimed is:

1. In a method for the electrolysis of aqueous chloride brines using an anode having a platinum metal surface, the improvement of (1) activating said platinum metal surface by subjecting said surface to the action of alternating current of 25 to 80 hertz under a current density of from 0.5 to 6 amperes per square inch of platinum surface at a temperature of from 20 to 100° C. for at least 5 minutes in an aqueous electrolyte in which chlorides are substantially absent and (2) electrolyzing aqueous chloride brine using the thus activated anode.

2. Method as claimed in claim 1 in which said platinum metal surface is supported on titanium.

3. Method as claimed in claim 2 in which said platinum metal is platinum.

4. Method as claimed in claim 1 in which said electrolyte is sulfuric acid.

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