GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 95423, application No. 95423 dated 31st August 1964. Complete Specification left on 26th May, 1965. Application accepted 28th February 1966.

PROVISIONAL SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO ETCHING OF TANTALUM.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Old Mill Road, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification describes the nature of this invention.

This is an invention by BALKUNJE ANANTHA SHENOI, Scientist, KANDADAI RAJAGOPALACHARI NARASIMHAN, Senior Scientific Assistant and KUSHAIMANNAM LAKSHMANA IYER RAMACHANDRAN, Junior Laboratory Assistant, all of the Central Electrochemical Research Institute, Karaikudi-3, India, all Indian citizens.

This invention relates to improvements in etching of Tantalum.

Hitherto it has been proposed to use d.c. for etching Tantalum to obtain a favourable etch ratio for use in capacitors.

This is open to the objection that the etch ratio is fairly low and can be improved by other methods.

The object of this invention is (i) to obviate these disadvantages by using super imposed a.c. over d.c. so that the etch ratio is increased; & (ii) to provide improved capacitors employing etched tantalum electrodes giving higher etch ratio, ranging from atleast 7 to 15.

To these ends, the invention broadly consists in etching tantalum in a methanolic solution of NH_4X, where X is Cl, Br, F or CNS containing a small percentage of water. A d.c. current with a definite fraction of a.c. super-imposed is passed through the electrolyte at temperature 20 to 35° C.

The following typical examples are given to illustrate the invention:

Example 1.

Electrolyte: 12 g of NH_4CNS in 1000 ml. of methanol containing 10 to 20 ml. of water.

Temperature: 32° C.

With Tantalum as anode and aluminium stainless steel or any other metal as cathode an etch ratio of about 12-15 was obtainable when a d.c. current with superimposed a.c. was employed.

Example 2.

Electrolyte: 12 g of NH_4Br in 1000 ml. of methanol containing 5 to 10 ml. of water.

Temperature: 32° C. Etch duration: 10 min.; C.D.: 4 to 10 A/dm^2.

With Tantalum as anode and aluminium as cathode, an etch ratio of about 7 to 10 was obtained when a d.c. current with superimposed a.c. was employed.

The following are among the main advantages of the invention:

Tantalum being a costly metal, it is important that a maximum surface area per unit weight be obtained in order that the amount of tantalum per unit of capacitance shall be a minimum. Some of the advantages of tantalum capacitors over aluminium capacitors are its stable electrical characteristics and longer shelf life with a reduction in size.

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Patents Officer.

Council of Scientific & Industrial Research.

Dated this 24th day of August 1964.

COMPLETE SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO ETCHING OF TANTALUM.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Old Mill Road, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This is an invention by BALKUNJE ANANTHA SHENOI, Scientist, KANDADAI RAJAGOPALACHARI NARASIMHAN, Senior Scientific Assistant and KUSHAIMANNAM LAKSHMANA IYER RAMACHANDRAN, Junior Laboratory Assistant, all of the Central Electrochemical Research Institute, Karaikudi-3, India, all Indian citizens.

The invention relates to a method of etching tantalum for use as anodes in electrolytic capacitors. Electrolytic capacitors made out of tantalum are known for their stable electrical characteristics and long shelf life. The metal is costly and has to be imported and hence it is desirable to obtain a maximum increase in surface area per unit weight.

A few firms have started manufacturing aluminium electrolytic capacitors with foreign know-how and so far no one has introduced or have started manufacturing tantalum capacitors. A few patents are there in foreign countries for etching tantalum for use as capacitor anodes, but the method claimed in this patent is novel and gives very high etch ratios hitherto not reported in literature.

Etching material increases the effective surface area of the electrodes and thereby correspondingly increases the electrical capacity per unit of projected area or the capacity value for a given electrode size. This increase may be expressed as the "etch ratio", which may be defined as the ratio of the capacitance of the etched surface formed at a particular voltage to the capacitance of a plain surface also formed at the same voltage having the same geometric area.

The method described in the application comprises electrolytically etching tantalum in an electrolyte comprising a solvent like methanol and an inorganic soluble salt containing fixed quantity of water using direct current superimposed with a.c.

As for the salt component of the bath, it is essential that the said component in the composition of the solution should bring about only etching and not film formation on the tantalum used as anode during electrolytic etching. Methanol has a greater solubility for inorganic substances and hence a wide concentration can be employed and is limited only by the solubility of that particular substance. Examples of suitable substance are the halides, thiocyanates of sodium, potassium and ammonium and organic halogen acids like trichloroacetic acid.

Better etching is obtained by having small quantity of water in the electrolyte described earlier and the water content though not very critical, does influence the etch ratio and hence has to be controlled within the permissible limits which varies with the nature of the soluble substance used with methanol.

Etching is considerably improved by using direct current superimposed with a.c. The ratio increases as

the a c component of the a c, d c mixture increases and also with the nature of the electrolyte It is possible to obtain very high etch ratios by this method, but it is equally important not to lose the mechanical strength of the foils which are intended for subsequent rolling up operations during fabrication of the capacitors This maximum etch ratio without losing the mechanical strength varies with the nature of the electrolyte The etch ratio decreases with forming voltage and we could get an etch ratio of more than four when formed at 200 Volts

The following examples illustrate the process

EXAMPLE 1.

200 ml of A R methanol containing 1 0 ml of water with 2 4 g of ammonium chloride dissolved in it was used as the electrolyte The direct current component current density range for obtaining high etch ratio is 25-40 ma/cm² Different a c/d c ratios were obtained by increasing the a c component suitably The variation of etch ratio as the a c/d c ratio increases is given below The duration of etching for all the experiments is 10 minutes The etched foils were formed at 30 V

a c/d c ratio	E R
0 625	6 4
0 75	7 2
0 87	8 8
1 0	9 6
1 25	10 4
1 5	10 8
1 75	11 2
2 0	11.2

EXAMPLE 2

200 ml of A R methanol containing 1 1 ml of water with 2 4 g of ammonium bromide dissolved in it was used as the electrolyte The variation of etch ratio with increase of a c/d c ratio is as given below Other conditions are as given in example 1

a c/d c ratio	E R
0 625	4 8
0 75	5 2
0 87	6 8
1 0	7 1
1 25	8 4
1 5	10 0
1 75	11 2
2 0	11 2

It is possible to get an etch ratio of 9 5 at 75 V by the examples illustrated above and the variation of the etch ratio as the forming voltage increases is as given below

Formation voltage	E R
100	7 4
150	6 4
200	4 7

It is not necessary to have any elaborate set up for obtaining the a c superimposed d c The single phase rectifiers generally available in the laboratory can be employed with success

EXAMPLE 3

The following example illustrates the use of single phase full wave rectifier

Electrolyte consists of a solution of 2 4 gms of NH_4Cl in 200 ml of AR methanol The current density employed is 35 ma/cm² and the following table illustrates the use of the current source for etching Duration of etching is 10 minutes

Expt No.	Amount of water ml/200 ml	E R
1	0	7.5
2	0 1	9 0
3	0 4	10 0
4	0 8	8 4
5	1 0	8 0
6	1 5	8.0
7	2 5	7 4
8	3 0	6 0
9	4 0	2 0

It has been noticed that the water content in methanol is not so critical and the range which gives the maximum etch ratio is fairly wide and this is illustrated by the following example

EXAMPLE 4

Electrolyte	Current source	Quantity of ml/ litre water needed for obtaining high E R	Max etch ratio obtainable
2 4 g NH_4Br in 200 ml methanol	Battery for the d c	0 to 4	>3
„	Single phase rectifier	3 5 to 15	>6
2 4 g NH_4CNS in 200 ml of A R methanol	Battery	8 0 to 20	>4
„	Single phase rectifier	5 to 25	>8

Since the range of water content giving the maximum etch ratio is fairly wide, it may not be necessary to use absolute methanol or AR methanol for this work Distilled methanol may be enough for the purpose provided the water content is known

We claim

1 A method of etching tantalum in an electrolyte solution consisting of methanol or any other organic solvent, a methanol-soluble inorganic salt or organic halogen acid and water with a c superimposed d c. current

2 A method of etching tantalum in an electrolyte of the type referred in (1) with a c superimposed d c current, the current density, d c component being in the range of 25-40 ma/cm²

3 A method of etching tantalum in an electrolyte referred under (1) with a c superimposed d c the current density of d c portion being 25 40 ma/cm² and the ratio of a c/d c being in the range of 0 37 to 1 5

4 A method of etching tantalum in an electrolyte referred under (1) with a current source from a single phase rectifier which gives the a c/d c ratio in the range referred under (iii)

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Dated this 19th day of May 1965

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