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IMPROVEMENTS IN OR RELATING TO ETCHING OF ALUMINIUM OR ITS ALLOYS FOR USE AS ELECTRODES IN ALUMINIUM ELECTROLYTIC CAPACITORS

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH RAFI MARG, 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, Scientist, VENKATASUBRAMANIAN LAKSHMINARASIMHAN, Senior Scientific Assistant, VIJALAKSHMI RAMAKRISHNAN, Senior Laboratory Assistant and Miss LAKSHMI SIVASWAMY, Senior Laboratory Assistant, all of the Central Electrochemical Research Institute, Karaikudi-623006, Tamil Nadu, India, all Indian citizens.

This invention relates to improvements in or relating to etching of super pure aluminium of purity 99.99% for use as anode or its alloy having a purity of 99.4% to 99.98% for use as cathode in electrolytic capacitors. Electrolytic capacitors are known for their small size and the capacity per unit volume is sufficiently high compared to paper, ceramic or other types of capacitors. This high capacitance to volume ratio is made possible by the use of etched foils.

Hitherto it has been proposed to treat the foil anodically in soluble chloride solution using pure DC or AC superimposed DC or square wave or DC current with various percentages of pulsation.

This is open to the objection in that etching in conventional sodium chloride electrolyte using pure DC does not give etch ratio of more than 12 at 15 volts. AC super imposed DC involves the use of AC having a frequency of more than 130 cycles per second and having a high degree of pulsation. So, special generators for the AC source as well as suitable filters and chokes are needed. Similarly, special type of equipment are required to produce square wave or pulsating DC. They are costly and probably will have to be imported if indigenous sources are not available.

The object of this invention is to obviate these disadvantages by a suitable process using DC and etching formulations to obtain high etch ratios.

The increase in surface area of the foil after etching operation is expressed in terms of etch ratio. Etch ratio is defined as ratio of capacitance of the etched foil to that of the plain foil of same geometrical area when formed and measured under identical conditions.

It is well known that when aluminium is made the anode in an aqueous solution containing a weak organic acid like tartaric, citric or their soluble salts described by us in our earlier patent No. 100313 dated 29-6-1965 or inorganic substances like sulphuric, chromic or boric acids or their salts, an oxide film is formed depending upon the current density, temperature, duration etc. In the patent details described hereunder, these substances are referred to as film forming substances. We found that the addition of these substances either alone or in mixture to soluble chloride increases the surface area of the foil during electrochemical etching. By soluble chloride, we mean salts like potassium, ammonium, calcium, magnesium, aluminium etc.

According to the present invention, there is provided a process for electrochemical etching of aluminium or its alloys for use as electrodes in electrolytic capacitors by passing direct current in an aqueous solution of soluble chloride or hydrochloric acid as the main constituent and with one or more film forming compounds which are capable of producing oxide film on aluminium or its alloys during anodic oxidation. High etch ratio in the range of 20 to 22 is obtained.

Etching may be carried out in an aqueous solution containing soluble chloride or hydrochloric acid in the concentration range of 1% to 15% w/v and a film forming compound in the concentration range of 0.5% to 5% w/v with direct current at a current density ranging between 0.16 A/cm² and 0.64 A/cm². The temperature of the aqueous electrolyte is maintained at 85°C to 100°C during the process of etching.

The film forming compounds such as malonic, succinic, maleic, oxalic, citric acids or mineral acids like chromic, sulphuric, boric acid or salts like sodium hydrogen sulphate, ammonium dihydrogen orthophosphate is added either alone or as mixtures to the soluble chloride solution.

Thus, the process involves in electrochemical etching of aluminium and its alloys using direct current in aqueous electrolyte having soluble chloride and substances capable of giving an oxide film over aluminium.

The investigation is carried out as follows:

Super pure aluminium foil of purity 99.99% or its alloy of purity 99.5% is anodically etched in two litres of etching solution using stainless steel as cathode. Etching is carried out with direct current obtained from a three-phase rectifier. A current density in the range of 0.16 A/cm² to 0.64 A/cm² is applied to the foil for a period of 60 to 140 seconds depending upon the nature of the electrolyte. The foil is then washed with tap water and subsequently with deionised water.

It is then anodised to 15 volts with direct current in a forming electrolyte containing 0.1% dihydrogen ammonium ortho-phosphate at 85°C till a minimum leakage direct current of 100-125/μA/sq. in. for super pure aluminium (99.99%) and 600-700/μA/sq. in for aluminium alloy of purity 99.5% is obtained. In the case of the latter, it is difficult to get a leakage current less than 500/μA/sq. in. even after anodising for a considerable period.

The capacitance is measured in a capacitance bridge at 12 volts in a measuring electrolyte containing 12.0 gm/litre of ammonium pentaborate at room temperature whose resistance is adjusted to 120 ohms by adding ammonia dropwise. The aluminium foil used as cathode for measuring is treated with 10% sodium hydroxide solution kept at 40°C for two minutes and washed with tap water and then with deionised water.

The etch ratio values stated in the examples are calculated by dividing the capacitance of the etched foil with the capacitance of the plain foil of the same geometrical area when both the foils are formed and measured under identical conditions.

The following typical examples are given to illustrate the invention:

EXAMPLE 1

Electrolyte : 200 g of sodium chloride and 20g of dihydrogen ammonium Temperature: phosphate in 2 litres of water. 98°C.

Etching is carried out using super purity aluminium (99.99%) as anode and stainless steel as cathode at a current density of 0.6 A/cm² for 60 seconds.

Etch ratio obtained is 17 at 15 volts.

EXAMPLE 2

Electrolyte : 200 grams of sodium chloride and 100 grams of malonic acid in 2 litres of water.

Temperature : 98°C

Etching is carried out using super pure aluminium (99.99%) as anode and stainless steel as cathode at a current density of 0.425 A/cm² for 65 seconds.

Etch ratio obtained is 17 at 15 volts.

EXAMPLE 3

Electrolyte : 200 grams of sodium chloride and 140 grams of chromic acid in 2 litres of water.

Temperature : 100°C.

Etching is carried out using super pure aluminium (99.99%) as anode and stainless steel as cathode at a current density of 0.48 A/cm² for 85 seconds. The etch ratio obtainable is 22 at 15 volts.

EXAMPLE 4

Electrolyte : 200 grams of sodium chloride and 140 grams of chromic acid in 2 litres of water.

Temperature : 100°C

Etching is carried out using alloy of aluminium (99.5%) as anode and stainless steel as cathode at a current density of 0.48 A/cm² for 85 seconds. The etch ratio obtainable is 22 at 15 volts.

EXAMPLE 5

Etching is carried out with alloy of aluminium (99.5%) of salts obtained by reacting monoethanolamine and citric acid in 2 litres of water.

Temperature : 98°C.

Etching is carried out as indicated in Example 3 using super pure aluminium (99.99%) and the etch ratio obtainable is 22 at 15 volts.

EXAMPLE 6

Electrolyte : 200 grams of table salt and 100 grams of commercial purity sodium sulphate and 10 grams of oxalic acid are dissolved in 2 litres of water.

Temperature : 98°C.

Etching is carried out with super pure aluminium (99.99%) as anode and stainless steel as cathode at a current density of 0.44 A/cm² for 100 seconds.

Etch ratio obtained is 21 at 15 volts.

EXAMPLE 7

Electrolyte : 200 grams of table salt and 100 grams of commercial purity sodium sulphate and 10 grams of oxalic acid are dissolved in 2 litres of water.

Temperature : 98°C.

Etching is carried out with alloy of aluminium (99.5% as anode and stainless steel as cathode at a current density of 0.4 A/cm² for 100 seconds. Etch ratio obtained is 21 at 15 volts.

EXAMPLE 8

Electrolyte : 200 cc of hydrochloric acid (conc.) + 100 cc of lactic acid and the total volume made upto 2 litres.

Temperature : 98°C.

Etching is carried out with super pure aluminium (99.99%) as anode and stainless steel as cathode at a current density of 0.58 A/cm² for 85 seconds. The etch ratio obtained is 18.5 at 15 volts.

EXAMPLE 9

Electrolyte: 200 grams of sodium chloride and 100 grams of sodium sulphate (com.) in 2 litres of water.

Temperature: 98°C

Etching is carried out with aluminium alloy of 99.5% purity as anode and stainless steel as cathode using conditions as described in Example 3. An etch ratio of 18.0 is obtained when formed at 15 volts.

The following is the main advantage of this invention

It is possible to obtain etch ratio of 20-22 by adopting a suitable process using d.c., correct composition and etching conditions and thereby effect considerable reduction in the volume/size of the capacitor which is a main trend in the miniaturisation of electronic components.

We claim:

1. A process for electrochemical etching of aluminium or its alloys for use as electrodes in electrolytic capacitors by passing direct current in an aqueous solution of soluble chloride or hydrochloric acid as the main constituent and with one or more film forming compounds which are capable of producing oxide film on aluminium or its alloys during anodic oxidation to get high etch ratio in the range of 20 to 22.

2. A process as claimed in claim 1 wherein etching is carried out with direct current at a current density range of 0.16 A/cm² to 0.54 A/cm².

3. A process as claimed in claim 1 wherein etching is carried out in a solution containing soluble chloride or hydrochloric acid in the concentration range of 1% to 15% w/v.

4. A process as claimed in claim 1 wherein the film forming compounds such as malonic, maleic, succinic, oxalic, citric acids or mineral acids like chromic, sulphuric, boric acids or salts like sodium hydrogen sulphate, ammonium dihydrogen orthophosphate is added to the soluble chloride solution either alone or as mixture in the concentration range of 0.5% to 5% w/v.

5. A process as claimed in claim 1 wherein the temperature of the aqueous electrolyte is maintained in the range of 85°C to 100°C during the process of etching.

Dated this 24th day of August, 1973.

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