This is an invention by BALKUNJE ANANTHA SHENOI, Scientist, KANDADAI RAGHOPALACHARI NARASIMHAN, Scientist, VENKATASUBRAMANIAN LAKSHMINARASIMHAN, Senior Scientific Assistant, VIJALAKSHMI RAMAKRISHNAN, Senior Laboratory Assistant and Miss LAKSHMI LAXMY, 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 alloys having a purity of 99.9% 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 a solution containing sodium 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 anodic current 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 hydrosulphate, ammonium dichromate or phosphates are added either alone or as mixtures to the soluble chloride solutions.

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

In this invention, the foil is then washed with tap water and subsequently with deionised water.

It is then anodised to 15 volts with direct current in an forming electrolyte containing 0.1% dihydroxy ammonium oxo-chromate at 35°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 g/litre of ammonium pentaborate at room temperature whose resistance is adjusted to 420 ohms by adding ammonium dropwise. The aluminium foil used as a 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 ratio of 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: 300 g of sodium chloride and 30 c of dihydrogen phosphonate in 2 litres of water.
Temperature: 98°C.
Etching is carried out using super purity aluminium (99.9%) as anode and stainless steel as cathode at a current density of 0.625 A/cm² for 60 seconds.
Etch ratio obtained is 17 at 15 volts.

EXAMPLE 2

Electrolyte: 200 gms of sodium chloride and 100 gams 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 gams of sodium chloride and 140 gams of chronic 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 0.68 A/cm² for 85 seconds. The etch ratio obtainable is 22 at 15 volts.

EXAMPLE 4

Electrolyte: 200 gams of sodium chloride and 140 gams of chronic 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 (99.9%) of salts obtained by reacting molybdenum trioxide 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 gams of table salt and 100 gams of commercial purity sodium sulphate and 10 gams 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 gams of table salt and 100 gams of commercial purity sodium sulphate and 10 gams 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. Each ratio obtained is 21 at 15 volts.

EXAMPLE 8

Electrolyte: 200 c of hydrochloric acid (conc.) + 100 c of lactic acid and the total volume made up to 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 0.28 A/cm² for 85 seconds. The etch ratio obtained is 18.5 at 15 volts.

EXAMPLE 9

Electrolyte: 200 gams of sodium chloride and 100 gams of sodium sulphate (com.) in 2 litres of water.
Temperature: 90°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 where 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 anodic 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.

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