Title: SOLID ELECTROLYTIC CAPACITOR AND METHOD FOR MANUFACTURING THE SAME

Abstract: A method of using a mask (20, 20') comprising a plurality of perforations (22, 22') for producing a plurality of porous anode bodies (42) is described. The method comprises using an electrophoretic deposition process (EPD) to deposit particles of an electrically conducting, dielectric-oxide film-forming material onto a substrate made from an electrically conducting, dielectric-oxide film-forming material located at the bottom of the perforations in the mask. The size and shape of the green anode bodies are defined by the size and shape of the perforations in the mask. Also described is the method of carrying out the additional steps required to produce solid electrolytic capacitors from the green anode bodies.
SOLID ELECTROLYTIC CAPACITOR AND METHOD FOR MANUFACTURING THE SAME

5 Field of Invention
The present invention generally relates to solid electrolytic capacitors. More particularly, the present invention relates to volume efficient solid electrolytic capacitors featuring a high ratio of anode volume to total capacitor volume. Also, the present invention relates to a process based upon electrophoretic deposition as the preferred manufacturing route for such electrolytic capacitors.

Background of the Invention
In order to facilitate the reading of the description to follow, a number of terms employed in the art are defined below:

- Primary Particle: The small volume of solid material having the same bulk density (measured in unit mass per unit volume) as said material. "Primary particles" are often referred to as "particles" or as "solid particles" herein.

- Agglomerate or granule: A collection of primary particles bonded by surface or interface forces and, when necessary, binder materials into a disordered cluster.

- Capacitor Grade Powder: A collection of pure primary particles and granules or agglomerates having defined chemical and physical properties and commercially suited for the manufacture of solid electrolytic capacitors.

- Capacitor Grade Powder Particles: A collection of pure primary particles having defined chemical and physical properties and
commercially suited for the manufacture of solid electrolytic capacitors.

- Green Body: A porous body manufactured from primary particles, granules or agglomerates, packed together and bonded by surface forces and (optionally) binder additives. Green bodies have low mechanical strength and a mass density appreciably less than the bulk density of the primary particles.

- Particle Size: An average diameter of a collection of particles, sometimes defined as the cube root of the particle volume. \( D_{10} \) denotes the apparent measured particle diameter below which 10% of the measured particle volume is to be found, \( D_{50} \) is the median measured particle diameter by volume. \( D_{90} \) is the measured particle diameter below which 90% of the measured particle volume is to be found.

- Sintered Body: A body having appreciable mechanical strength and formed by heating a green body in a known atmosphere at a sufficiently high temperature and for long enough time to allow mass transfer and particle bonding. Sintering usually involves a reduction in pore volume, associated with shrinkage of the green body and an increase in apparent density.

- Volumetric Efficiency of Electrical Capacitance: The electrical capacitance per unit volume of the sintered anode in a solid electrolytic capacitor.

- Effective surface area: The total area of the open pore structure that corresponds to the interconnected free surface of the partially bonded particles relative to the total surface area of the pore structure, which may also include closed as well as open pores.

- The porosity of a green or sintered body is defined as the volume fraction occupied by pores or voids in the body relative to the total volume, defined by the external dimensions of said body.
- The theoretical density is the density of the material present in the absence of pores, that is, when 100% of the volume of the body is occupied by a solid phase.

- A valve-metal is a material which forms a uniform stable oxide on its surface. Examples of valve-metals are: tantalum, aluminum, magnesium, titanium, niobium, zinc, zirconium or niobium monoxide.

Small equipment size, characteristic of the mobile phone industry, personal computers, cameras, hearing aids and mobile office equipment, drives the market demand for a high component packaging density on printed circuit boards. To respond to this challenge, especially for high frequency performance, solid electrolytic chip capacitors are designed to provide low manufacturing costs, small product dimensions, low height profile, a wide range of electrical capacitance, stable operation and extremely low values of parasitic ESR (equivalent series resistance), DCL (direct leakage current) and ESL (equivalent series inductance); thereby, enabling the design of more compact end-products for increased convenience and portability.

Solid electrolytic capacitors, available with various forms of encapsulation, feature higher electrical capacitance in package sizes, which are small when compared to other types of capacitors. Due to their high volumetric efficiency and reliability, miniature 'chip' solid electrolytic capacitors are especially suitable for surface mounting (SMT) applications and are increasingly being used in current microelectronics and communication applications.

A solid electrolytic capacitor consists of a high surface area, porous sintered pellet, the anode, made from capacitor grade powders, with an embedded or attached wire or foil conductor and a dielectric oxide layer, which is usually formed by anodizing the anode open-pore surface. The thickness of the
dielectric layer is minimized and the open-pore surface area is maximized in order to achieve large capacitance. The high open porosity surface area of the pellet is the dominant feature that allows the solid electrolytic capacitor to have better volumetric efficiency than any other type of capacitor. The anodized porous body is subsequently impregnated with a cathode material, and then connected to a cathode lead wire or frame. The final assembly is encapsulated in epoxy or other resin.

Anodes of solid electrolytic capacitors made from the metals tantalum (Ta), niobium (Nb) and aluminum (Al) dominate today’s markets. Newer types of anode made from niobium oxide (NbO) have been developed and commercialized in recent years. Solid electrolytic capacitors made of NbO have excellent electrical properties, high reliability and low manufacturing costs.

The effective capacitive efficiency of any given capacitor powder is usually evaluated by a single ‘lumped’ parameter, the CV for the powder, which is the product of the theoretical capacitance for a given powder particle size distribution and the formation voltage for the dielectric oxide per unit powder weight. CV has the physical units of micro-Farads multiplied by volts divided by grams. The capacitive efficiency increases as the effective specific surface area of the anode increases. The green capacitor anode is usually made from highly porous granules of an agglomerated fine powder. The two features that control penetration of any open pore network, such as that in the green capacitor anode, are the number of channels connecting the pores and the diameter of the connecting channels. An open pore structure is essential for the formation of the dielectric on the anode surface. Also the pore channel distribution must be optimized for impregnation of the cathode material. The optimal pore structure and distribution is difficult to achieve.
By way of example only, common aspects of some powders currently used for
the production of solid electrolytic capacitors are given below. Because
unagglomerated powders have very poor flow properties, the processing of
capacitor grade powders commonly includes agglomeration by spray drying.
The agglomerated granules permit automatic and reliable green anode
production by the conventional method of cold pressing. However, powder
agglomeration degrades the electrical properties of the powders, and
reduces the CV of the powders.

**Capacitor Grade Tantalum and Niobium Powders**

US Patent No. 5,986,877 and US Patent No. 5,954,856 both describe
methods of making tantalum metal powder with controlled size distribution
and also sintered tantalum capacitor anodes produced from said tantalum
powder, by compressing agglomerates of said tantalum powder. The primary
particles of the powders from which the agglomerates are made, may have
an average particle size ranging between 0.1 micron and about 5 microns.
By comparison, the agglomerated tantalum powder has a size distribution
with a granule size of a few tens of microns to a few hundreds of microns.

STA-80 KA (Product number: 01014629) is a 80 KCV (1000CV= 1KCV)
capacitor grade tantalum powder made by H.C. Starck. According to the
manufacturer’s data, the powder contains at least 99 wt% of Ta. Thereported average size of the agglomerates ranges from 1.5 to 2.3 micron with
79% of the agglomerated particles smaller than 38 microns, 17.9% of the
agglomerates between 38 microns and 63 microns, 1.7% between 63 microns
and 106 microns, 0.8% between 106 microns and 150 microns and 0.1%
between 150 microns and 300 microns. This powder has a specific surface
area of 1.7 square meters per gram (m^2/g).
Capacitor grade tantalum powders, made by Cabot Corporation (www.cabot-corp.com), are available with KCV values ranging from 10 to 70. The powders are agglomerated with a mean particle size near 10 micron and an agglomerated mean granule size of around 400 to 600 microns.

US Patent No. 6,765,786 discloses a niobium powder for producing niobium capacitors. The powder has a size distribution from 10 microns to 200 microns.

**Capacitor Grade Niobium Monoxide**

US Patent No. 6,527,937 describes a method for producing capacitor grade niobium monoxide powder. Examples of the powder shapes that can be used include flaked, angular, nodular and a mixture of these, all having a particle or granule size ranging from a few tens of microns to few hundreds of microns.

Typical properties published by Herman Starck, the manufacturer of 80 KCV NbO powder, show a wide agglomerate size distribution. A maximum of 10% of all diameters are below 38 microns, 5 to 15% are between 38 microns and 63 microns, 10 to 20% are between 63 microns and 100 microns, 25 to 35% are between 100 microns and 150 microns, 25 to 35% are between 150 microns and 200 microns, 5 to 15% are between 200 microns and 300 microns. The powder has a specific surface area between 1.05 and 1.25 m²/g.

In one method of producing a solid electrolytic capacitor known from the prior art, the agglomerated powder is first mixed with specified adhesive binders, and pressed to form a ‘slug’ having a density appreciably lower than the bulk density of the anode material. The slug is sintered in vacuum at about 1500°C to form a rigid capacitor anode with high open porosity and
good mechanical strength. After sintering, a dielectric oxide layer is formed by anodizing the interconnected open porosity of the anode. The thickness of the dielectric layer is directly proportional to the anodization formation voltage. Next a cathode is formed on the surface of the dielectric by impregnating a cathode material, such as manganese oxide (MnO₂), or a conductive polymer. Good electrical contact with the cathode requires that the cathode material should conform to the surface micro-topology of the convoluted oxide layer previously formed on the open porosity of the anode.

Another method of manufacturing a capacitor known from the art, which is more appropriate for manufacture of miniature electrolytic capacitors, is described in patent US 6,673,389 and elsewhere. This method starts from a solid tantalum substrate. Coarse grained capacitor grade tantalum powder is first sintered onto the substrate as a bonding layer. This is followed by a pressed green layer of capacitor grade powder. After sintering of the green layer, transverse and longitudinal grooves are machined in the substrate to produce an orthogonal grid of the sintered bodies, and this is followed by dielectric formation. A resist layer is applied along the grooves, surrounding the sintered anode bodies and masking any underlying tantalum oxide layer formed on the exposed substrate surface. A manganese dioxide cathode is then impregnated. This is followed by application of a conducting carbon and silver coat. Shallow cuts are made along the center line of each channel, removing a thin layer of resist and any excess cathode material. The channels between the capacitor bodies are then filled with epoxy resin, followed by slicing through the remaining thickness of the tantalum substrate to separate each capacitor body from its neighbors. External metallization of the capacitor body is completed using standard processes such as electroplating.
It is desirable that the geometrical shape of the anode should resemble that of the capacitor package. Since wire-connection and lead-frame assembly of prior art electrolytic capacitors occupy a large volume fraction of the capacitor package, box-shape capacitor anodes without wires and lead frames can facilitate efficient utilization of the available volume of the capacitor package, to achieve a high capacitance density in the final package.

Due to the limitations of the state of the art, manufacturing processes for the smallest solid electrolytic capacitors commercially available have a 0402 (~1mm x ~0.5mm x ~0.5mm) case size, providing a maximum capacitance of ~10μF at 3V rating. There are presently two major limiting factors on the available capacitance of capacitors having such small case sizes. The first is the poor volume efficiency of the capacitor. This can be seen in Fig. 1, which is a photomicrograph showing a cross section of a typical prior art capacitor. The capacitor shown in Fig. 1 is a TACmicrochip™ Capacitor manufactured by AVX Corporation. The specifications of the capacitor are: R case – 0805 (2.00 x 1.35 x 1.35 mm), 15μF, 4V rating. In the example shown, the volume ratio of the anode to the total capacitor volume is only ~30%. The second limiting factor is the prior art method of forming the green anode by pressing, which prevents the use of powders with CV values above ~150KCV since these fine powders are difficult to process by pressing.

A goal of the art is to manufacture solid electrolytic chip capacitors from fine non-agglomerated particles and to utilize the open channels and large surface area intra-pore structure to produce capacitors having high capacitance efficiency, low ESR and improved DCL. The currently employed methods of manufacturing anodes for solid electrolytic capacitors are not able to process fine particles effectively or to manufacture efficiently ultra-
miniature electrolytic capacitors, down to 0201 size (0.6mm x 0.3mm x 0.3mm).

It is, therefore, an object of the present invention to make feasible a solid electrolytic capacitor having a small package size, high volumetric electrical capacitance, low ESR and low DCL.

It is another object of the present invention to provide a green body having defined geometry and a controlled degree of open porosity.

It is still another object of the present invention to use said green body to create a sintered body having a defined geometry and controlled degree of open porosity.

It is still another object of the current invention to provide an anode for a solid electrolytic capacitor using said sintered body.

It is still another object of the present invention to provide an anode for a solid electrolytic capacitor made from an oxide film-forming electrical conductor, wherein the morphology of the anode has a controlled open pore structure, in which the pores have a uniform structure with a narrow size distribution of pore diameters in order to achieve optimal cathode material impregnation.

It is still another object of the present invention to provide a miniature anode for a solid electrolytic capacitor having certain specific dimensions of length, width and thickness; preferably the dimensions of the anode are only slightly smaller than the capacitor that is constructed from it, providing volume efficiency of electrical capacitance of at least 50%.
It is a further object of the present invention to provide a miniature solid electrolytic capacitor using said capacitor anode.

It is a still further object of the present invention to produce the anode from a non-agglomerated, non-granulated capacitor grade powder, said powder to be made from fine particles of a dielectric-oxide, film-forming conductor material.

It is a still further object of the present invention to provide a solid electrolytic capacitor cathode made from any suitable cathode material, including but not limited to manganese oxide and a conductive polymer.

It is a still further object of the current invention to provide a manufacturing process for solid electrolytic capacitor anodes using capacitor grade powders.

Other objects and advantages of the invention will become apparent in the following description of this invention.

**Summary of the Invention**

Tantalum, niobium and niobium oxide anodes of electrolytic capacitors are manufactured in accordance with the prior art by cold pressing granulated powder into green bodies followed by sintering. This is true for the longstanding prior art method of cold pressing individual pellets and also for more recent techniques of cold pressing powder onto a substrate, sintering and then dicing to individual anodes, as taught in US 6,673,389.

As opposed to the prior art methods, the method of the present invention uses electrophoretic deposition (EPD) to pack powder into a preformed mask in order to form the anode body. This production route is based on the
observation that the EPD process is able to fill cavities, providing that the bottom of the cavity is conductive and that an appropriate electric field is applied across the mask. By masking a valve-metal foil with a thick perforated sheet or plate of an electrically insulating material, wherein the thickness of the mask corresponds to the length of the capacitor, a large array of anodes can be produced in a batch processing sequence that can be continued nearly to the end of the manufacturing process. In another embodiment of this method, a small foil substrate is inserted into each of the perforations of the masking plate. This method and its various embodiments avoid the problems associated with the stressed sintered substrate and the metal dicing processes that accompany the method taught in US 6,673,389. The method of the present invention requires significantly less handling of the individual devices than the longstanding method of cold pressed pellet production.

Further advantages of the method of the invention are:

- Close dimensional tolerances can be achieved for the anode, since these are primarily determined by the mask dimensional tolerances, since the sintering shrinkage is nearly negligible.

- Since far less stress is present, thinner valve-metal foil may be used as the anode substrate in the method of the invention compared to the prior art process of dicing anodes from a sintered porous substrate. The use of thinner valve-metal support foil implies a greater volume available for the capacitor anode, corresponding to higher capacitance values per unit volume.

According to some embodiments of the invention, the capacitor bodies are kept as an array throughout much of the production process, including application of a 5-sided termination, solderable coating to the ends of the
capacitors. Hence fixtureing for low cost mass production is very efficient and handling of bulk chips is only required from the barrel plating stage through to the end of the process sequence.

In a first aspect the invention is a method of using a mask comprising a plurality of perforations for producing a plurality of porous green anode bodies. The method comprises using an electrophoretic deposition process (EPD) to deposit particles of a electrically conducting, dielectric-oxide film-forming material onto a substrate made from an electrically conducting, dielectric-oxide film-forming material located at the bottom of the perforations. The size and shape of the green anode bodies is defined by the size and shape of the perforations in the mask. The method of the invention comprises the following step:

(a) providing the mask;
(b) attaching the mask to the substrate, such that there is electrical continuity between the bottoms of all of the perforations;
(c) preparing a stable suspension for EPD by dispersing a known weight of the electrically conducting, dielectric-oxide film-forming material in a known amount of dispersion medium together with certain chemical additives;
(d) immersing the mask attached to the substrate in an EPD cell containing the suspension;
(e) carrying out the EPD process until the perforations are filled with the particles; and
(f) removing excess deposited material leaving the finished porous green anode bodies flush with the surface of the mask.

According to preferred embodiments of the invention, the mask is made from an elastomeric plastic, rubber, or a ceramic material. The sides of the perforations in the mask can be either straight or tapered. In different
embodiments the horizontal cross-section of the perforations can be square, rectangular, circular, or elliptical.

In preferred embodiments of method of the invention the substrate is made from an electrically conducting, dielectric-oxide film-forming material selected from the group comprising: tantalum, aluminum, magnesium, titanium, niobium, zinc, zirconium, niobium monoxide, stoichiometric or non-stoichiometric, or alloys of these materials. In a preferred embodiment, the substrate comprises an extended, continuous foil attached to the mask such that it covers the bottoms of the plurality of the perforations in the mask, thereby allowing the parallel production of a plurality of anode bodies on the same substrate foil. In another embodiment the substrate comprises small pieces of foil, which are precut to the shape and size of the bottoms of the mask cavities and one of each of the pieces is inserted into the bottom of each perforation of the mask. In this embodiment the mask is attached to a conductive backing plate, thereby providing electrical continuity between all of the pieces of foil and allowing the parallel production of a plurality of anode bodies using the mask.

According to the method of the invention the particles of electrically conducting, dielectric-oxide film-forming material may have any CV value and are selected from the group comprising: tantalum, aluminum, magnesium, titanium, niobium, zirconium or niobium monoxide, stoichiometric or non-stoichiometric, or alloys of these materials.

In another aspect, the method of the invention comprises an additional step (g) of sintering the porous green anode bodies, thereby producing a plurality of sintered anode bodies. The porous green anode bodies are removed from the mask before a sintering treatment or, if the mask is a ceramic mask made of a material that does not bind to the porous green anode bodies
during high-temperature vacuum-sintering, the sintering treatment can be performed with the porous green anode bodies in the mask.

In yet another aspect, the method of the invention comprises an additional step (h) of anodizing the sintered anode bodies, thereby producing a plurality of sintered capacitor anodes. If the sintering has been done with the porous green anode bodies in the mask, then the anodizing to form a dielectric layer on the sintered anode body can also be carried out before extraction of the anode body from the mask.

In preferred embodiments of the invention, the anode bodies are bonded to a carrier foil to allow subsequent process steps to be performed on multiple anode bodies rather than on individual units.

In still another aspect, the method of the invention comprises additional steps, which allow the production of a plurality of solid electrolytic capacitors from the sintered capacitor anodes. The additional steps are:

(i) cathode formation;

(j) encapsulation;

(k) coating with barrier and seed layers;

(l) separating the capacitors from each other; and

(m) barrel plating with nickel and tin.

According to the method of the invention, cathode formation comprises the steps of impregnating and coating the anode bodies with conducting or semiconducting materials, which in preferred embodiments are chosen from the group comprising: manganese dioxide, a conductive polymer, and both of these materials. In a preferred embodiment, an external conductive carbon coating is applied following the steps of impregnating and coating the anode
bodies and a silver coating can be deposited onto the conductive carbon coating.

In one embodiment of the method of the invention, the encapsulation is done by dipping the cathode-covered anode bodies into a dilute solution of an encapsulation polymer. In another embodiment the encapsulation is done by depositing a vacuum-based conformal coating material on the cathode-covered anode bodies. A preferred vacuum-based conformal coating material is parylene.

In a preferred embodiment of the method of the invention the barrier and seed layers are applied by a vacuum deposition process.

In the method of the invention in which the plurality of porous green anode bodies are formed on an extended, continuous foil substrate, after the capacitors are produced the substrate is sectioned by a laser, in order to remove excess substrate material, thereby separating the capacitors.

All the above and other characteristics and advantages of the invention will be further understood through the following illustrative and non-limitative description of preferred embodiments thereof, with reference to the appended drawings.

**Brief Description of the Drawings**

- Fig. 1 is SEM micrograph showing a cross-section of a tantalum capacitor made by the method of the prior art;
- Fig. 2A schematically shows a cross section of a mask made from a plastic or rubber sheet;
- Fig. 2B schematically shows a cross section of a mask made from a ceramic sheet;
- 16 -

- Fig. 2C shows schematically a perforated mask bonded to a valve-metal foil;
- Fig. 3A and Fig. 3B illustrate one method of inserting the valve-metal pieces into the mask cavities;
- Fig. 4A and 4B show cross sectional views of the mask after its perforations have been filled with green electrophoretic slugs deposited on the valve-metal foil by the EPD process;
- Figs. 5A and 5B show cross sectional views of the mask after excess deposited material protruding above the level of the top surface of the mask has been removed;
- Fig. 6 shows a method for removing the green electrophoretic bodies from a silicone rubber or other elastomeric mask;
- Fig. 7A shows the sintered bodies attached to carrier foil by a temporary conductive adhesive layer;
- Fig. 7B shows the sintered bodies after formation of the dielectric oxide and attached to valve-metal foil, which acts as a carrier foil;
- Figs. 8A and 8B show respectively the carrier foil and the valve-metal foil with sintered bodies attached and covered by the thin masking sheet;
- In Figs. 9A and 9B show the sintered bodies of Figs. 8A and 8B after impregnation of cathode material and application of a cathode layer;
- Figs. 10A and 10B show the formation of the encapsulation material on the sintered bodies shown in Figs. 9A and 9B respectively;
- Figs. 11A and 11B show the structure of Fig. 10A, after the rubber or elastomeric sheet and the carrier foil have been removed, respectively before and after coating with the barrier and seed layers;
- Figs. 12A and 12B show the steps in applying the barrier and seed layers to the capacitors that are held in a perforated plate;
- Fig. 13 shows the finished capacitor; and
Fig. 14 is an optical micrograph showing a cross-section of a green tantalum anode made by the method of the invention.

**Detailed Description of the Preferred Embodiments**

Fig. 1 is a SEM micrograph showing a cross-section of a tantalum capacitor made by the prior art technique of pressing agglomerated tantalum powder granules onto a tantalum substrate followed by sintering, dicing, dielectric formation, manganese dioxide cathode impregnation, carbon and silver coating, encapsulation and external electrode metallization. The dimensions of the anode pellet shown in the figure are about 1.3 mm by about 1 mm. Attached to the ends of the pellet are tantalum substrates, a thinner substrate 12 at the cathode end and a thicker substrate 14 at the anode end. The encapsulating layer 16 around the anode pellet is about 0.2 mm thick. Volume efficiency of the capacitor, defined by the ratio of the anode volume to the total capacitor volume, is about 32%.

In accordance with the present invention, the production of a solid electrolytic capacitor begins with the provision of a mask comprising a matrix of perforations in which the anodes of the capacitors will be created. The mask is made from a perforated sheet of material such as plastic, preferably an elastomer, silicone rubber, or a ceramic, for example alumina. The width and depth of the perforations correspond closely to the dimensions of the capacitors to be produced. Fig. 2A schematically shows a cross section of a mask 20 made from a plastic, rubber, or other elastomeric sheet. Fig. 2B schematically shows a cross section of a mask 20' made from a ceramic sheet. For the elastomeric sheet shown in Fig. 2A, the sides of the perforations 22 are straight; however, for the ceramic mask 20', the sides of the perforations 22' are preferably slightly tapered in order to remove the mask after the anodes are formed. As an example, if a 0603 size capacitor is to be produced, cavity 22 in mask 29 would have a nominally square cross
section of 0.75x0.75mm and an approximate height of 1.5mm. For the same size capacitor, Cavity 22' would have a square bottom 0.8x0.8mm, a square top 0.7x0.7mm, and a nominal height of 1.5mm. It is to be noted that the figures are illustrative only and that although a mask having only four columns of perforations is portrayed, the inventors visualize much larger masks allowing the production of hundreds or even thousands of anodes from a single mask. In addition, the perforations in the mask can have horizontal cross-sections other than the square shape illustrated. For example, they could have rectangular, circular, or elliptical cross sections, which would result in cylindrically or elliptically shaped anodes.

In the next step, shown schematically in Fig. 2C, the perforated mask 20,20' is attached to a valve-metal foil (substrate) 24. The mask can be attached to the foil by any appropriate means, for example by using an adhesive or vacuum clamping, if the foil is sufficiently thin or the mask elastomeric.

In another embodiment of the invention, small pieces of valve-metal foil are precut to the shape and size of the bottoms of the mask cavities. One of each of these pieces will be inserted into each mask cavity as described hereinbelow and will act as the substrate on which the anode body will be deposited.

Fig. 3A and Fig. 3B illustrate one method of inserting the valve-metal pieces into the mask cavities. A plate 30 comprising a matrix of shallow recesses 32 is provided. The matrix of recesses 32 matches the matrix of perforations 22,22' in the mask 20,20'. There is preferably a hole 36 through the bottom of the plate 30 at the center of each recess 32 to facilitate transfer of the valve-metal pieces to the mask.

The valve-metal pieces 34 are shaken into the array of recesses 32 on plate 30. A mask 20,22' with matching perforations is placed over the matrix of
valve-metal pieces on the plate 30. The bottoms of the perforations in the mask are slightly smaller than the valve-metal pieces. Plate 30 with overlying mask 20,22' is placed over another plate that comprises an array of short pins that fit the holes 36 in the center of each recess 32 in plate 30. A press or vacuum is then used to force the valve-metal pieces 34 into the ends of the mask perforations 22,22' as shown in Fig. 3B. Finally the mask is separated from plate 30 and placed over another metal plate 42 (see Fig. 4A) and held in place by a clamp, such that the valve-metal plates are in contact with the conductive backing plate 42.

The mask perforations are then filled with a valve-metal powder such as tantalum, niobium or niobium oxide using electrophoretic deposition (EPD). Methods of using EPD processes to deposit electrodes on wires and foils for use in electrolytic capacitors are described in co-pending published U.S. Patent Application No. 2004-0195093 and in International Patent Application No. PCT/IL2004/000865, both by the same applicant, the descriptions of which, including reference cited therein, are incorporated herein by reference in their entirety.

The capacitor grade powder used in the present invention can be made from any electrically conductive, anodic dielectric-oxide film-forming material. According to preferred embodiments of the present invention, the powder is made from, but is not limited to, particles of one of the following materials: tantalum, aluminum, magnesium, titanium, niobium, zirconium or niobium monoxide, stoichiometric or non-stoichiometric, or alloys of these materials. According to another embodiment of the present invention, the capacitor grade powder used in this invention is made of fine, non-agglomerated particles of these materials. In preferred embodiments of the present invention, the capacitor grade powder used in this invention has a high chemical purity and contains at least 99% by mass of the electrically
conducting, dielectric-oxide film-forming material. In other embodiments of the present invention, the powder contains at least 99.5% by mass of this constituent. The capacitor grade powder to be used in this invention is selected from a group of capacitor grade powders that may have any CV value.

In some embodiments of the present invention, the measured powder aggregated particle size is characterized by D_{10} ranging from 0.4 micron to 2 microns, D_{50} ranging from 0.6 micron to 4 microns and D_{90} ranging from 4 microns to 8 microns. According to other embodiments of the present invention, the measured aggregated powder particle size is characterized by D_{10} ranging from 0.5 micron to 0.8 micron, D_{50} ranging from 0.8 micron to 2 microns and D_{90} ranging from 1.5 microns to 4 microns.

A stable suspension for EPD is prepared by dispersing a known weight of capacitor grade powder in a known amount of polar solvent medium together with certain chemical additives. The additives inhibit agglomeration of the capacitor-grade aggregated powder particles, stabilize the suspension and control its electrophoretic properties. For the purposes of this invention, a suspension is said to be 'stable' when the rate of EPD significantly exceeds the rate of sedimentation of the solids content under gravity, and the particle size distribution in suspension remains effectively unchanged throughout the electrophoretic deposition cycle time. A stable suspension requires that the measured zeta potential of the particles in suspension, that is, the effective electrical charge on the suspended particles, be sufficiently high (up to about ±30mV) and that the pH and electrical conductivity remain effectively independent of the deposition time. In preferred embodiments of the invention the electrical conductivity is no greater than 4.0 micro-Siemens/cm and the pH is adjusted to obtain the required zeta potential.
The dispersion medium used in this invention may be a commercially pure polar solvent, selected from a group of polar solvents, or a mixture of two or more polar solvents, or a mixture of one polar solvent with one or more non-polar solvents. According to preferred embodiments of the present invention, the dispersion medium used in the present invention should have a dielectric constant equal to or larger than 6 and a chemical purity of at least 99%.

The solids loading for suspensions in the present invention is defined as the mass of capacitor grade powder per unit volume of solvent and ranges from 1 gram per liter to 1000 grams per liter. In some preferred embodiments the solids loading ranges from 10 grams per liter to 200 grams per liter and in more preferred embodiments from 50 grams per liter to 100 grams per liter.

According to a still further embodiment of the present invention, the dispersion medium in the present invention is selected from the group of solvents including, but not limited to water, methyl alcohol, ethyl alcohol, n-propyl alcohol, butyl alcohol, pentyl alcohol, isopropyl alcohol, nitromethane, acetonitrile, dimethyl ketone, methyl ethyl ketone, diethyl ketone, dichloromethane and dichloroethane.

Soluble additives for dispersions used in the present invention can be selected from three classes of chemical substances. The first of these classes of additive, for the sake of simplicity termed in this invention 'charging agents', inhibit aggregation of the capacitor grade powder particles by creating electrostatic repulsion between the particles in suspension. The second class of additives, for the sake of simplicity termed in this invention 'steric additives', inhibit aggregation of the capacitor grade powder particles through steric hindrance between the powder particles. The third class of
additives, for the sake of simplicity termed in this invention 'electro-steric additives', inhibit aggregation of the capacitor grade powder particles by a combination of both electrostatic repulsion and steric hindrance between the powder particles.

In different embodiments of the present invention, electrosteric additives, a mixture of steric additives and charging agents, or a mixture of steric additives and electrosteric additives are selected to stabilize the dispersion.

Chemical substances in the class of electrosteric additives include, but are not limited to, polyethylenimine, quaternary ammonium salts and phosphate ester compounds. Chemical substances in the class of charging agents include, but are not limited to, nickel(II) chloride hexahydrate, nickel acetylacetonate, cobalt(II) acetylacetonate and aluminum chloride hexahydrate. Chemical substances in the class of steric additives include, but are not limited to, dodecyl sodium sulfate and polyethylene glycol.

According to some embodiments of the present invention, the concentration of chemical additives, selected from the classes of charging agents, steric additives and electrosteric additives, is between 0.1 micro-liters of additive dissolved in 100 milliliters of solvent, to 1 milliliter of additive dissolved in 100 milliliter of solvent. In other embodiments, the concentration ranges between 5 microliter of additive in 100 milliliter of solvent, and 500 micro-liters of additive in 100 milliliter of solvent.

According to the present invention, EPD of the green anode body can be carried out in an electrophoretic deposition cell that generates a well-controlled electrical field in the dispersion. According to a preferred embodiment of the present invention, the electrical field at the deposition
electrode for EPD of the green anode body ranges from 1 volt per centimeter to 300 volts per centimeter.

According to the present invention, EPD to form the green anode body can be at a controlled, constant electric current passing through the deposition cell.

In some embodiments of the invention, the green electrophoretic slug is removed from the mask prior to sintering. In these embodiments the electrophoretic deposition is preferably done with an added organic binder to increase anode green strength. Alternately, the mask with the green electrophoretic slug can be placed in an organic binder solution so that binder impregnates the green pore structure and increases green strength upon drying. Other embodiments of the invention employ a ceramic mask and the green electrophoretic body is sintered while still in the mask. In these embodiments the use of minimum quantities or no binder is preferred.

After the EPD process is completed, excess anode material is removed to leave the finished green slug flush with the surface of the mask. Figs. 4A and 4B show cross sectional views of the mask 20, 20' with its perforations filled with green electrophoretic slugs 40 that have been deposited on the valve-metal foil 24, 34 by the EPD process. Figs. 5A and 5B show cross sectional views of the mask 20, 20' after the excess EPD anode material has been removed in the finishing process.

After the deposition and finishing process, the green electrophoretic bodies are removed from the plastic or rubber masks before they are sintered. In the case of a ceramic mask, the green electrophoretic bodies may be sintered in the mask, if the ceramic providing the mask material does not bond to the electrophoretic body during high-temperature vacuum-sintering.
A method for removing the green electrophoretic bodies from a rubber or elastomer mask is shown in Fig. 6. This method is applicable to the embodiment in which the deposition was on individual substrates of valve-metal foil inserted into the perforations in a silicone rubber mask. In this case the mask containing the green electrophoretic slugs is attached to an adjustable frame that grips the mask edges. Means are provided to extend the length of the sides of the frame, thereby evenly stretching the mask. The mask perforations are then larger than the green bodies so the bodies fall from the mask with minimal assistance, for instance, by gentle vibration of the rubber mask.

The green electrophoretic slugs are now sintered, either as individual units on the valve metal inserts (embodiment of Fig. 5B), or in place on the valve-metal foil (embodiment of Fig. 5A), or in place in the ceramic mask.

According to the present invention, sintering of the green anode body is performed in a vacuum furnace or a furnace having a controlled inert gas atmosphere. The temperature in the sintering furnace can range between 600 degrees Celsius and 2000 degrees Celsius. In preferred embodiments of the present invention, using tantalum or niobium oxide the sinter temperature is between about 1000 to 1400 degrees Celsius.

In the embodiment where the electrophoretic bodies are deposited through a mask onto individual valve-metal foil inserts or substrates, then removed from the mask and sintered as individual units, it is preferred to bond the sintered bodies to a carrier foil to allow subsequent process steps to be performed on multiple bodies rather than individual units. One method for mounting the sintered bodies prior to subsequent processing is to shake the sintered bodies through a suitable mask onto a foil made of aluminum or
other conductive material that has been coated with an uncured, conductive adhesive on one side and an insulating masking material on the other side. The carrier foil may also be coated with a thin layer of valve-metal on one side, in which case the uncured, conductive temporary adhesive is applied on top of the thin valve-metal coating.

Slight asymmetry between the two ends of the electrophoretic body resulting from possible tapering of the body and/or the presence of the substrate at the anode end may be exploited to orient the bodies so that they can be bonded to the carrier foil at the end with the valve-metal substrate. A positioning device comprising a matrix of openings is provided. Since the end of the body with the valve-metal substrate is slightly larger than the opposite end, if the openings in the positioning device are slightly smaller than the larger end then shaking the anodes into the positioning device will organize all of the bodies with the valve-metal substrate facing up. When all of the openings contain a sintered body, the positioning device is flipped over onto the side of the carrier foil coated with uncured conductive adhesive, in order to bond the bodies to the foil. Fig. 7A shows the sintered bodies 42 attached to carrier foil 44 by a temporary conductive adhesive layer (not shown) between the carrier foil 44 and the valve-metal substrate 34.

In the embodiment where the electrophoretic bodies are deposited and sintered on a sheet of a continuous valve-metal foil, the valve-metal foil also acts as a carrier substrate. In this case the back of the valve-metal foil may be masked prior to subsequent process steps. Fig. 7B shows the sintered bodies 42 attached to the valve-metal foil 24, which acts as a carrier foil.

The sintered electrophoretic bodies on the carrier foil are next immersed in an anodizing solution, using the composition and process conditions known
to those skilled in the art, thereby forming a dielectric oxide layer on all interconnected surfaces within the porous structure of the sintered electrophoretic body. Preferably, any coating or contamination is removed from the carrier foil between the electrophoretic bodies prior to the dielectric formation process. Alternatively, the exposed carrier foil surface between the electrophoretic bodies may be electrically isolated by any known means prior to the process of forming the dielectric layer.

When the bodies have been deposited through a ceramic mask and sintered while in the mask dielectric formation may be performed prior to removal of the bodies from the mask. In this case, a metal plate is brought into close electrical contact with the valve-metal foils embedded in the ceramic mask by using a suitable mechanical fixture which provides electrical contact for the dielectric formation process to all of the electrophoretic bodies. After dielectric formation, the anode bodies are extracted from the ceramic mask by applying an adhesive backing foil or plate to the valve-metal substrate of the anode bodies and lifting the ceramic mask away from the anode bodies.

Prior to cathode formation, a thin perforated rubber or plastic sheet that is held in place by a wire frame or an adhesive masking layer is attached to mask the valve-metal or carrier foil between the anode bodies. The carrier foil and anode bodies are then dipped into cathode solution or dispersion and processed by means known to those skilled in the art. The cathode preparation process includes impregnation and coating by manganese dioxide or conducting polymer, followed by an external coating with carbon paste and silver paste. The carrier foil 44 and the valve-metal foil 24, with sintered bodies 42 attached and covered by the thin masking sheet 46, are shown in Figs. 8A and 8B respectively. In Figs. 9A and 9B are shown the sintered bodies of Figs. 8A and 8B after the cathodes 48 have been formed.
After cathode formation the upper masking layer or sheet 46 is removed, leaving the valve-metal foil 34,24 and the ends of the anode bodies 42 isolated from the cathode material 48. A rubber or elastomeric sheet is placed over the cathode-coated ends of the anode bodies and mechanically held in place with a suitable frame. The frame is dipped into a dilute solution of an encapsulation polymer and excess liquid is drained before drying. The rubber or elastomer sheet is then removed and the encapsulation coating is cured. This process may be repeated if necessary in order to achieve the required thickness of protective coating, typically ~10μ.

Alternatively, a vacuum-based conformal coating material such as parylene may be used for polymer encapsulation.

Figs. 10A and 10B show the rubber or elastomer sheet 52 placed over the cathodes 48 and the layers of encapsulation material 50 on the sintered bodies shown in Figs. 9A and 9B respectively.

After encapsulation, the free ends of the capacitor bodies are coated with barrier layers and seed layers in preparation for nickel and tin barrel plating. The nickel and tin end coatings constitute the external electrodes of the capacitor, which are used to attach the capacitor to electrical circuits. The barrier and seed coatings may be produced by vacuum deposition such as evaporation or sputtering. Barrier layers may be chromium, silver or other metals. Seed layers may be copper, nickel or other metals.

In the embodiments wherein the electrophoretic bodies were deposited onto individual valve-metal foil inserts or substrates and later attached to a carrier foil such as aluminum, the carrier foil and its adhesive layer are removed by chemical etching, solvent dissolution, or heating. If encapsulation was by applying a thick parylene coating, then an intact free parylene film remains in place after removal of the rubber or elastomer
sheet. This free film leaves the cathode end of the capacitor exposed while effectively masking the rest of the capacitor body during the barrier and seed layer vacuum deposition process. In this case, the excess free parylene films and barrier and seed layer over-coating are removed from between the capacitor bodies after the vacuum deposition. The removal process may use known techniques such as flame, hot-wire, laser and etching processes to remove the free film without significant damage to either the encapsulation or the end coatings that are bonded to the capacitor bodies.

Figs. 11A and 11B show respectively the structure of Fig. 10A, after the rubber or elastomer sheet 52 and the carrier foil 44 have been removed, before and after coating with the barrier and seed layers 56.

If the encapsulation process does not leave a free standing film that can be used as a vacuum deposition mask, then the capacitor end coatings of barrier and seed layers are accomplished by bulk-vibrating the capacitors into an appropriate holder for vacuum coating, which is a method known to those skilled in the art.

In the embodiments wherein the electrophoretic bodies were deposited through a mask onto a continuous valve-metal foil sheet, barrier and seed layers may be deposited onto the ends of the capacitors using a process whereby a perforated metal plate is lowered over the encapsulated capacitor bodies while they are still attached to the continuous valve-metal foil. The perforations are designed to fit closely over the capacitor bodies with a minimal gap that will allow the metal plate to be lowered over the capacitor bodies. The thickness of the plate is designed to allow approximately 0.1mm to 0.2mm of the end of the capacitor body to project beyond the plate. The bottom surface of the plate is chamfered to a depth of typically 0.1 to 0.2mm to ease insertion of the capacitors, and to define subsequently the external
electrode area at the other end of the capacitors.

In this embodiment, barrier and seed layer coatings are first formed on the cathode end of the capacitor and then formed on the opposite end of the capacitors by inverting the perforated plate so that the supporting valve-metal foil is uppermost. A computer-controlled laser may be used to cut the valve-metal foil at the edges of the capacitors. The excess foil is then lifted away from the capacitors, while applying a vacuum hold-down to keep the capacitors in position in the perforated plate. Vacuum coating of barrier and seed layers is then performed on the end cap of valve-metal foil remaining on each capacitor after laser cutting. Figs. 12A and 12B show the steps in applying the barrier and seed layers 56 to the capacitors that are held in perforated plate 54.

After release from the perforated plate or being separated from each other a number of known processes are subsequently performed on the barrier and seed layer coated capacitors in order to complete the manufacture of the capacitor. These steps include:

- Barrel plating with nickel and tin, thereby completing the capacitor external electrodes, known as terminations.
- Sorting the capacitors by capacitance, typically into bins of 5% tolerance, 10% tolerance and 20% tolerance.
- Packing the capacitors for automated assembly onto electrical circuits, a packing process known as Tape & Reel. The packing machine will preferably provide the following features:
  - Machine vision that identifies the small geometrical difference between the two ends of the capacitor and consistently orients the capacitors in the tape, for example by using a rotating disc, so that all capacitors will be oriented with the anode electrode in one direction.
and the cathode in the opposite direction. The two ends will not be identical since one end is terminated by a piece of valve-metal foil while the second is not. Machine vision can also be used to eject any capacitors that are detected to have defects such as those based on dimensional tolerances and gross surface defects e.g. incomplete termination.

- Optionally, laser marking can be used to provide a mark near the anode termination and a value code at the center of the capacitor.

- Ability to measure capacitance and other electrical characteristics to verify compliance with the specification and to eject the capacitor if it does not comply.

- Ability to insert the capacitor into the tape.

The following examples are provided merely to illustrate the invention and are not intended to limit the scope of the invention in any manner.

**Example 1: Production of NbO anode and dielectric oxide layer**

**Powder selection**

The powder used in this example is 60-80KCV capacitor grade NbO powder supplied by Ultra*Mat LTD (Israel) and manufactured by Ningxia CO. LTD (China). Chemical analysis, performed by the manufacturer, shows that the powder used in this example has the following chemical composition, excluding Niobium:

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<th>Element</th>
<th>Abundance</th>
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<tr>
<td>C</td>
<td>35</td>
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<tr>
<td>O</td>
<td>15</td>
<td>wt%</td>
</tr>
<tr>
<td>Fe</td>
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Cr  <30  ppm
Ni  <30  ppm
Al  <30  ppm
Mg  160  ppm
5  Mn  <30  ppm
Na  10  ppm
K   10  ppm
Si  <30  ppm
Ti  <30  ppm
10 N   450 ppm
H   60  ppm
P   10  ppm
Cu  <30  ppm

15 Physical properties and screen analysis data of the powder supplied by the manufacturer:
   Scott density (g/cc):  1.25
   Fisher size (μm):     4.78
   BET (m²/g):           1.48

20 Screen analysis:
   Mesh          wt%
   -60/+80        13.64
   -80/+150       67.90
   -150/+325      14.60
   -325/+400      3.86

25 The aggregate particle size distribution after ultrasonic treatment to break down soft powder agglomerate as measured was: D10(μm)=1.706, D50(μm)=3.56, D90(μm)=154.10.

30 Preparation of NbO suspension
A 200 grams per liter NbO suspension was prepared by mixing 20 grams of NbO powder in 100 milliliters of 2-propanol (Manufacturer: Bio-Lab, Jerusalem, Israel, grade: PEPTIDE synthesis, Cat number: 162633). The suspension was sonicated (Vibracell, output power: 750 Watt, frequency: 20 kHz, 19 mm solid tip probe) for 5 minutes at 80% amplitude, with a 2 seconds on / off pulse rating. The suspension was cooled during sonication and the suspension temperature did not exceed 35 degrees Celsius. 320 microliter of a 17% by weight aqueous solution of polyethylenimine (Sigma-Aldrich, St. Louis, Missouri, USA, Cat. Number 48,259-5) was prepared and added to the suspension. Then, the suspension was again sonicated for 1 minute at 80% amplitude, using a 2 seconds on / off pulse rate. The suspension was cooled during sonication and the suspension temperature did not exceed 35 degrees Celsius. After that, the suspension was magnetically stirred for 30 minutes.

The pH, measured at 21 degrees Celsius after 30 minutes of magnetic stirring, was 9.5 and the electrical conductivity was 0.5 micro-Siemens per centimeter.

**Preparation of NbO green anode body by EPD**

A 0.15 mm thickness tantalum foil that acted as anode, and a 2.5 cm by 2.5 cm by 1.5 mm thickness square alumina plate with a 0.8 mm x 0.8 mm central hole were mounted in close contact in a suitable jig. An external voltage of 500 volts was applied between the anode and a cathode counter-electrode in the presence of the suspension, and positively charged NbO particles were deposited on the surface of the tantalum foil and within the alumina hole. The deposition time required to fill the hole by EPD was 20 minutes. The green anode formed had a length of 1.5 mm and cross section of 0.8x0.8 mm.
Sintering of the EPD green anode

The green anode was sintered in a vacuum furnace at a pressure of 5×10⁻⁵ millibar and a temperature of 1250 degrees Celsius. The sintering cycle included heating from room temperature to 150 degrees Celsius, at a rate of 50 degrees Celsius per minute and then continued heating at a rate of 100 degrees Celsius per minute to the final sintering temperature. The dwell time at the final sintering temperature was 20 minutes, after which the furnace was switched off. As the temperature in the furnace reached room temperature, the furnace was pumped to 5×10⁻⁵ millibar and then back-filled with 50 millibar of air over an additional 20 minutes. The pressure was then raised to 100 millibar of air over an additional 20 minutes. Finally, air was admitted to atmospheric pressure and the furnace was opened.

Fig. 14 is an optical micrograph showing a cross-section of a green tantalum anode made by the method of the invention. To make the anode shown in Fig. 14, tantalum particles were deposited by EPD on the surface of a tantalum foil having a thickness of 150 microns, which was held in close contact with a 1.5 mm thick laser-drilled alumina mask. Dimensions of the mask perforation are 0.8 mm x 0.8 mm square with a 0.2 mm radius at the perforation corners. It should be noted that the pore structure revealed in the section of this green anode is homogeneous and the pores are distributed uniformly throughout the anode.

While some embodiments of the invention have been described by way of illustration, it will be apparent that in practice the invention can modified, varied or adapted, together with numerous equivalent or alternative embodiments that are within the capacity of persons skilled in the art, without departing from the spirit of the invention or exceeding the scope of the claims.
Claims

1. A method of using a mask comprising a plurality of perforations for producing a plurality of porous green anode bodies, said method comprising using an electrophoretic deposition process (EPD) to deposit particles of a electrically conducting, dielectric-oxide film-forming material onto a substrate made from an electrically conducting, dielectric-oxide film-forming material located at the bottom of said perforations, wherein the size and shape of said green anode bodies is defined by the size and shape of said perforations in said mask; said method comprising the steps of:

(a) providing said mask;
(b) attaching said mask to said substrate, such that there is electrical continuity between the bottoms of all of said perforations;
(c) preparing a stable suspension for EPD by dispersing a known weight of said electrically conducting, dielectric-oxide film-forming material in a known amount of dispersion medium together with certain chemical additives;
(d) immersing said mask attached to said substrate in an EPD cell containing said suspension;
(e) carrying out the EPD process until said perforations are filled with said particles; and
(f) removing excess deposited material leaving the finished porous green anode bodies flush with the surface of said mask.

2. A method according to claim 1, wherein the mask is made from a material selected from the group comprising:

(a) an elastomeric plastic;
(b) rubber; and
(c) ceramic.
3. A method according to claim 1, wherein the sides of the perforations in the mask are selected from the group comprising:
   (a) straight sides; and
   (b) tapered sides.

4. A method according to claim 1, wherein the horizontal cross-section of the perforations is selected from the group comprising:
   (a) square;
   (b) rectangular;
   (c) circular; and
   (d) elliptical.

5. A method according to claim 1, wherein the substrate is made from an electrically conducting, dielectric-oxide film-forming material selected from the group comprising: tantalum, aluminum, magnesium, titanium, niobium, zinc, zirconium, niobium monoxide, stoichiometric or non-stoichiometric, or alloys of these materials.

6. A method according to claim 5, wherein the substrate comprises an extended, continuous foil attached to the mask such that it covers the bottoms of the plurality of the perforations in said mask, thereby allowing the parallel production of a plurality of anode bodies on the same substrate foil.

7. A method according to claim 5, wherein the substrate comprises small pieces of foil, which are precut to the shape and size of the bottoms of the mask cavities and one of each of said pieces is inserted into the bottom of each perforation of the mask.
8. A method according to claim 7, wherein the mask with a piece of foil inserted into the bottom of each of its perforations is attached to a conductive backing plate, thereby providing electrical continuity between all of said pieces of foil and allowing the parallel production of a plurality of anode bodies using said mask.

9. A method according to claim 1, wherein the particles of electrically conducting, dielectric-oxide film-forming material may have any CV value and are selected from the group comprising: tantalum, aluminum, magnesium, titanium, niobium, zirconium or niobium monoxide, stoichiometric or non-stoichiometric, or alloys of these materials.

10. A method according to claim 1, comprising an additional step, thereby producing a plurality of sintered anode bodies said step comprising:
   (g) sintering.

11. A method according to claim 10, wherein the porous green anode bodies are removed from the mask before a sintering treatment.

12. A method according to claim 10, wherein the mask is a ceramic mask made of a material that does not bind to the porous green anode bodies during high-temperature vacuum-sintering, thereby allowing said sintering treatment when said porous green anode bodies are in said mask.

13. A method according to claim 10, comprising an additional step, thereby producing a plurality of sintered capacitor anodes, said step comprising:
   (h) anodizing.
14. A method according to claim 12, wherein the dielectric layer is formed on the sintered anode body using an anodization process, before extraction of said anode body from the mask.

15. A method according to claim 7, wherein the anode bodies are bonded to a carrier foil to allow subsequent process steps to be performed on multiple anode bodies rather than individual units.

16. A method according to claim 13, comprising additional steps, thereby producing a plurality of solid electrolytic capacitors, said steps comprising:

(i) cathode formation;
(j) encapsulation;
(k) coating with barrier and seed layers;
(l) separating said capacitors from each other; and
(m) barrel plating with nickel and tin.

17. A method according to claim 16, wherein cathode formation comprises the steps of impregnating and coating the anode bodies with conducting or semiconducting materials.

18. A method according to claim 17, wherein the impregnating and coating material is chosen from the group comprising: manganese dioxide, a conductive polymer, and both of these materials.

19. A method according to claim 17, wherein an external conductive carbon coating is applied following the steps of impregnating and coating the anode bodies.

20. A method according to claim 19, wherein a silver coating is deposited onto the conductive carbon coating.
21. A method according to claim 16, wherein the encapsulation is done by dipping the cathode-covered anode bodies into a dilute solution of an encapsulation polymer.

22. A method according to claim 16, wherein the encapsulation is done by depositing a vacuum-based conformal coating material on the cathode-covered anode bodies.

23. A method according to claim 22, wherein the vacuum-based conformal coating material is parylene.

24. A method according to claim 16, wherein the barrier and seed layers are applied by a vacuum deposition process.

25. A method according to claim 6, wherein the extended, continuous foil substrate is sectioned by a laser, in order to remove excess substrate material, thereby separating the capacitors.
Fig. 4A

Fig. 4B

Fig. 5A

Fig. 5B
Fig. 8A

Fig. 8B
INTERNATIONAL SEARCH REPORT

INTERNATIONAL APPLICATION NO
PCT/IL2006/000528

A. CLASSIFICATION OF SUBJECT MATTER
INV. H0164/12  H0169/15

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B32B  H01G  C03B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched.

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<tr>
<td>A</td>
<td>J. VAN TASSEL, AMIT DAGA, C A RANDALL: &quot;electrophoretic deposition for fabrication of ultra thin multi component electroceramic tapes&quot; INTERNATIONAL SYMPOSIUM ON MICROELECTRONICS, 1999, pages 647-652, XP009070662</td>
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<tr>
<td>A</td>
<td>WO 00/40398 A (THE PENN STATE RESEARCH FOUNDATION; RANDALL, CLIVE A; VAN TASSEL, JON) 13 July 2000 (2000-07-13)</td>
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Further documents are listed in the continuation of Box C.

See patent family annex.

Date of the actual completion of the international search
8 August 2006

Date of mailing of the international search report
17/08/2006

Name and mailing address of the ISA/
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Fax. (31-70) 340-3019

Authorized officer
Dessaux, C

Form PCT/ISA/2/10 (second sheet) (April 2005)
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