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(54) Title: POROUS SOLID OXIDE FUEL CELL ANODE WITH NANOPOROUS SURFACE AND PROCESS FOR FABRICATION

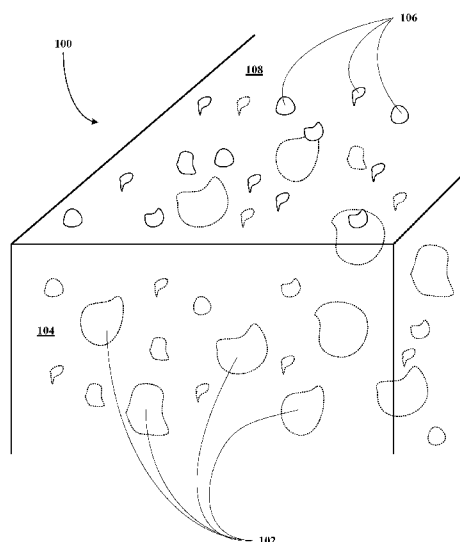


FIG. 1A

(57) Abstract: Electrochemical devices including solid oxide fuel cells (SOFCs) or thin film solid oxide fuel cells (TFSOFCs) having a porous metallic anode with nanoporous surface structure enabling the deposition of a dense, impermeable thin film electrolyte layer on the porous anode. Fabricating methods include forming a mixture of nanopowder metallic agents and nanopowder proppant that are sintered, smoothed and etched to form the nanoporous surface structure.



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PCT SPECIFICATION

TITLE: POROUS SOLID OXIDE FUEL CELL ANODE WITH NANOPOROUS SURFACE AND PROCESS FOR FABRICATION

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RELATED APPLICATIONS

[0001] This application claims priority to and the benefit of United States Provisional Patent Application Serial No. 62/110,997 filed 02/02/2015 (02 February 2015).

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0002] Embodiments of the present invention relate to electrochemical apparatuses including solid oxide fuel cells (SOFCs) and methods for making and using same.

[0003] More particularly, embodiments of the present invention relate to electrochemical apparatuses including SOFCs, where the SOFCs include thin film solid oxide fuel cells (TFSOFCs) including a porous metallic anode having a nano-porous surface structure and a micro-porous internal structure enabling deposition of a dense, impermeable, thin film, electrolyte layer on the porous anode surface, while maintaining anodic function. The present invention also relates to methods for making and using same.

2. Description of the Related Art

[0004] Fuel cells are energy-conversion devices that use an oxidizer (*e.g.*, oxygen or air) to convert chemical energy in a fuel (*e.g.*, hydrogen or low molecular weight hydrocarbons) into electrical energy. A solid oxide fuel cell (SOFC) generally comprises a solid electrolyte layer with an oxidizer electrode (cathode) on one side of the electrolyte and a fuel electrode (anode) on the **other** side. The electrodes are required to be porous, or at least permeable to the oxidizer at the cathode and the fuel at the anode, while the electrolyte layer is required to be dense so as to prevent leakage of gas across the layer. A thin film solid-oxide fuel cell (TFSOFC) has a thin electrolyte layer, on the order of 0.1 micrometers or microns (μ or μ m) to 5 μ m thick, as described, for example, in United States Pat. No. 6,645,656. The use of a thin electrolyte layer reduces the operating temperature significantly. A significant reduction in operating temperature increases the reliability of the fuel cell, and allows wider choices of materials for TFSOFC applications. Using the TFSOFC design may also reduce materials costs and reduce the volume and mass of the fuel cell for a given power output.

[0005] United States Pat. No. 6,645,656 discloses physical and chemical deposition techniques to

synthesize basic components of a TF SOFC consisting of an electrolyte thin film, *e.g.*, yttria stabilized zirconia (although a number of other oxide electrolytes could be utilized), a thin film cathode layer, *e.g.*, lanthanum, strontium cobalt oxide (although a number of other oxide cathodes could be utilized) both deposited on a porous metal anode, *e.g.*, nickel (although a number of other metal anodes could be utilized).

[0006] Thin film oxide deposition technologies such as pulsed laser deposition (PLD) or metal organic chemical vapor deposition (MOCVD) can be used for the deposition of the oxide electrolyte as well as for the conducting oxide cathode layer. PLD is an ideal vehicle to develop very thin films for TF SOFC applications, while MOCVD is good for large area thin film fabrication. Sputtering, evaporation, sol-gel, metal organic deposition (MOD), electron beam evaporation, chemical vapor deposition (CVD), molecular beam epitaxy (MBE), or other oxide film deposition techniques can also be used. For an effective thin film electrolyte layer having a thickness between 0.1 μm and 5 μm to be deposited onto the porous metal anode, it must be dense and impermeable to gas flow. Hence the deposition of the thin electrolyte layer onto the anode requires that the surface of the porous metal anode have a pore size that is equal to or less than the thickness of the electrolyte layer, thus allowing for full coverage and closure of the pores. The most common porous metallic-based anode materials for solid oxide fuel cells are nickel (Ni)-cermets prepared by high-temperature calcination of NiO and yttria-stabilized zirconia (YSZ) powders as described in United States Pat. No. 6,589,680 B1; United States Pat. No. 7,842,200 B2; in Suzuki et al, "Impact of Anode Microstructure on Solid Oxide Fuel Cells", Science, 325, pp. 852(2009); in Chen et al, "Hierarchically Oriented macroporous anode-supported solid oxide fuel cell with thin ceria electrolyte film", Applied Materials & Interfaces, 6, pp. 5130(2014); in Y. Liu and M. Liu, "Porous SOFC anode prepared by sublimation of an immiscible metal oxide during sintering", Electrochem and Solid State Letters, 9, pp. B25 (2006). High-temperature calcination is essential in order to reduce the nickel oxide to metallic nickel and thus form the necessary electronic conductivity and porosity in the anode structure.

[0007] While several anode structures and methods for making the anode structures are known, there is still a need in the art for anode structures and methods for manufacturing same, where the porous metallic anode with nano-porous surface structure and micro-porous internal structure enables the deposition of a dense, impermeable thin film electrolyte layer on the porous anode, while maintaining anodic function

SUMMARY OF THE INVENTION

Methods for Making

[0008] Embodiments of the present invention provide methods for making porous metal anode films, where the porous metal anode films include surfaces having a surface nanoporous structure and an

interior having an internal nanoporous structure. The surface nanoporous structure is characterized in that the structure includes pores having pore sizes equal to or smaller than a thickness of an electrolyte layer deposited on a surface of the porous metal anode film. The internal nanoporous structure is characterized in that the structure includes pores having pore sizes greater than or equal to the pore sizes of the surface nanoporous structure.

[0009] Embodiments of this invention provide methods for making solid oxide fuel cell (SOFC) porous anodes including combining a metallic nanopowder and a proppant nanopowder to form a nanopowder mixture. The methods also include pressing the nanopowder mixture at a temperature and pressure and for a pressing time sufficient to form a shape having a least one flat surface. The methods also include heating the shape at an elevated temperature, at a pressure and for a heating time sufficient to form an SOFC anode. The methods may also include cutting the SOFC anode into a SOFC anode film having a given thickness. The methods may also include polishing at least one surface of the SOFC anode or a SOFC anode film to form a smoothed surface SOFC anode. The methods may also include ion etching the smoothed surface of the smoothed surface SOFC anode to form an ion etched, smoothed surface SOFC anode.

[0010] Embodiments of the present invention provide methods for making thin film solid oxide fuel cell (TFSOFCs) including a porous metal anode film of this invention, an oxide electrolyte layer deposited on a surface of the porous metal anode film, and a cathode layer deposited on a surface of the electrolyte layer, where the electrolyte layer covers or substantially covers the anode film and has a thickness sufficient to prevent shorting of the TFSOFC.

Anodes, Anode Constructs, and Solid Oxide Fuel Cells

[0011] Embodiments of this invention provide solid oxide fuel cell (SOFC) porous anode compositions including a porous interior and a porous surface. The porous surface includes pores having pore sizes between about 10 nm and about 1000 nm (1 μ m) and has a surface roughness less than or equal to about 100 nm. The porous interior includes pores having pore sizes between about 10 nm and about 10 μ m and the surface.

[0012] Embodiments of this invention provide porous anode constructs including an anode layer having a porous interior and a porous surface and an electrolytic layer formed on a thereof, where the electrolytic layer is a continuous, dense, and electrically insulating thin film. The porous surface includes pores having pore sizes between about 10 nm and about 1000 nm (1 μ m) and has a surface roughness less than or equal to about 100 nm. The porous interior includes pores having pore sizes between about 10 nm and about 10 μ m and the surface. The electrolyte layer has a thickness and coverage of the anode layer sufficient to prevent shorting of a SOFC include an anode construct of this invention.

[0013] Embodiments of this invention provide solid oxide fuel cell (SOFC) constructs including an anode layer having a porous interior and a porous surface, an electrolytic layer formed on a thereof, and a cathode layer formed on the electrolytic layer, where the electrolytic layer is a continuous, dense, and electrically insulating thin film sandwiched between the anode layer and the cathode layer. The porous surface includes pores having pore sizes between about 10 nm and about 1000 nm (1 μ m) and has a surface roughness less than or equal to about 100 nm. The porous interior includes pores having pore sizes between about 10 nm and about 10 μ m and the surface. The electrolyte layer has a thickness and coverage of the anode layer sufficient to prevent shorting of the SOFC.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The invention can be better understood with reference to the following detailed description together with the appended illustrative drawings in which like elements are numbered the same:

[0015] **Figure 1A** depicts a schematic representation of a metal anode construct of this invention.

[0016] **Figure 1B** depicts a schematic representation of a SOFC or TFSOFC of this invention.

[0017] **Figure 1C** depicts a schematic representation of a porous metal anode of this invention.

[0018] **Figures 2A-C** depict embodiments of a process flow diagram for fabrication of nanoporous metal anode of this invention.

[0019] **Figures 3A-C** depict embodiments of another process flow diagram for fabrication of nanoporous metal anode of this invention.

[0020] **Figure 4** depicts an embodiment of a process flow diagram for fabrication of metal anode constructs including a nanoporous metal anode of this invention.

[0021] **Figure 5** depicts an embodiment of a process flow diagram for fabrication of SOFCs or TFSOFCs including a nanoporous metal anode of this invention.

[0022] **Figures 6A-C** depict scanning electron micrographs of the surface of the porous metal anode: (A) after high temperature processing, but not in the finished state; (B) after mechanical polishing of the sample (A); (C) after ion etching of sample (B) - process complete.

[0023] **Figure 7** depicts a scanning electron micrograph of the interior of the porous metal anode showing larger pores in the interior than at the surface (**Figure 6C**).

[0024] **Figure 8** depicts a scanning electron micrograph showing a dense and continuous electrolyte layer deposited on top of the nanoporous surface of the processed metal anode,

DEFINITIONS OF TERM USED IN THE INVENTION

[0025] The following definitions are provided in order to aid those skilled in the art in understanding the detailed description of the present invention.

[0026] The term "about" means that the value is within about 10% of the indicated value. In certain embodiments, the value is within about 5% of the indicated value. In certain embodiments, the value

is within about 2.5% of the indicated value. In certain embodiments, the value is within about 1% of the indicated value. In certain embodiments, the value is within about 0.5% of the indicated value. [0027] The term "substantially" means that the value is within about 5% of the indicated value. In certain embodiments, the value is within about 2.5% of the indicated value. In certain embodiments, the value is within about 1% of the indicated value. In certain embodiments, the value is within about 0.5% of the indicated value. In certain embodiments, the value is within about 0.1% of the indicated value.

[0028] The term "SOFC" means a solid oxide fuel cell.

[0029] The term "TFSOFC" means a thin film solid oxide fuel cell.

[0030] The term "YSZ" means yttria-stabilized zirconia.

[0031] The term "CMP" means chemical-mechanical polishing.

[0032] The term "sccm" means standard cubic centimeters per minute.

[0033] The term "MOCVD" means organic chemical vapor deposition.

[0034] The term "MOD" means electron beam evaporation.

[0035] The term "CVD" means chemical vapor deposition.

[0036] The term "MBE" means molecular beam epitaxy.

DETAILED DESCRIPTION OF THE INVENTION

[0037] The inventors have found that new methods or processes for fabricating porous metal anodes having a nanoporous structure at the surface may be implemented, where the methods or processes yield porous metal anode films that are capable of being fully and imperviously covered by a thin film electrolyte layer. These processes permit the fabrication of SOFCs or TFSOFCs including the porous metal anode of this invention covered with a thin electrolyte layer resulting in reduced operating temperatures of the SOFCs or TFSOFCs. The electrolyte layer is dense and pore-free to prevent gas leakage through it and to eliminate shorting of the SOFCs or TFSOFCs between the fuel cell anode and the fuel cell cathode. We have also found that porous electrodes may be used to increase the gas transport rate of the SOFCs or TFSOFCs of this invention. These requirements increase fabrication difficulties of TFSOFCs as the electrolyte layer generally has a thickness between 0.1 μm and 5 μm thick, yet still must totally cover the surface pores of the porous anode to prevent gas leakage and shorting across the electrolyte layer.

Methods for Making SOFC Anodes, Anode Constructs, SOFCs, and TFSOFCs

Anodes

[0038] Embodiments of the present invention broadly relates to porous metal anode fabrication processes including mixing a metallic nanopowder and a proppant or pore forming nanopowder to form a nanopowder mixture, where the metallic nanopowder includes particles having particle sizes

between about 10 nm and 1000 nm or 1 μm and the nanopowder proppant particles are adapted to keep the metallic nanopowder particles separated and to form pores in a resulting anode. The processes also include pressing the mixture under pressing conditions of pressing time, pressing temperature, and pressing pressure to form a pressed shape. The processes further include heating the pressed shape in an inert gas environment under heating conditions of heating time, heating temperature, and heating pressure sufficient to sinter the mixture and to decompose the proppant or pore forming particles in the pressed shape to form a metal anode composition having a porous surface and a porous interior, where the porous surface comprises nanopores having a size between about 10 nm and about 1000 nm or 1 μm .

[0039] In certain embodiments, the processes further include a surface smoothing process designed to further expose and define the surface nanopores and/or reduce surface roughness or improve surface smoothness.

[0040] In certain embodiments, the surface smoothing process comprises a polishing step adapted to smooth one or both surfaces of the pressed shape to form a porous anode including a surface or surfaces having a smooth surface characterized by a surface roughness of less than or equal to about 100 nm. In other embodiments, the smooth surface characterized by a surface roughness of less than or equal to about 50 nm.

[0041] In certain embodiments, surface smoothing process comprises a polishing step adapted to smooth one or both surfaces of the pressed shape to form an porous anode including a surface or surfaces having a smooth surface characterized by a surface roughness of less than or equal to about 100 nm and ion etching step applied to the smoothed surface or surfaces to open surface nanopores that may have been closed or plugged during the polishing step.

[0042] In certain embodiments, the polishing step comprises mechanical polishing. In other embodiments, the polishing step comprises chemical polishing. In other embodiments, the polishing step comprises chemical-mechanical polishing (CMP).

[0043] In certain embodiments, the surface pores of the anodes have pore sizes between about 10 nm and about 500 nm or 0.5 μm , the interior pores have pore sizes between about 10 nm and about 10 μm and the surface has a roughness of less than or equal to about 100 nm. In other embodiments, the surface pores of the anodes have pore sizes between about 10 nm and about 500 nm or 0.5 μm , the interior pores have pore sizes between about 10 nm and about 10 μm and the surface has a roughness of less than or equal to about 50 nm.

[0044] In certain embodiments, the metallic nanopowder comprises particles having particle sizes between about 10 nm and 500 nm and the proppant nanopowder comprises particles having sizes between from 10 nm and 1000 nm or 1 μm . In other embodiments, the metallic nanopowder

comprises particles having particle sizes between about 10 nm and 500 nm and the proppant nanopowder comprises particles having sizes between from 10 nm and 500 nm.

Anode Slabs

[0045] Embodiments of the present invention broadly relate to porous metal anode fabrication processes including mixing a metallic nanopowder and a proppant or pore forming nanopowder to form a nanopowder mixture, where the metallic nanopowder includes particles having particle sizes between about 10 nm and 1000 nm or 1 μm and the nanopowder proppant particles are adapted to keep the metallic nanopowder particles separated and to form pores in a resulting anode. The processes also include pressing the mixture under pressing conditions of pressing time, pressing temperature, and pressing pressure to form a pressed slab having at least one flat surface or portion thereof. The processes further include heating the pressed slab in an inert gas environment under heating conditions of heating time, heating temperature, and heating pressure sufficient to sinter the mixture and to decompose the proppant or pore forming particles in the pressed shape to form a sintered slab having a porous surface and a porous interior, where the porous surface comprises nanopores having a size between about 10 nm and about 1000 nm or 1 μm .

[0046] In certain embodiments, the processes further include cutting the sintered slab to form slices.

[0047] In certain embodiments, the slabs or thin slices may require further processing to yield a sufficiently smooth nanoporous surface so that the surface may be uniformly and continuously coated by an electrolyte layer.

[0048] In certain embodiments, the processes further include a surface smoothing process designed to further expose and define the surface nanopores and/or reduce surface roughness or improve surface smoothness.

[0049] In certain embodiments, the surface smoothing process comprises a polishing step adapted to smooth one or both surfaces of the slab or slices to form a porous anode including a surface or surfaces having a smooth surface characterized by a surface roughness of less than or equal to about 100 nm. In other embodiments, the smooth surface or surfaces are characterized by a surface roughness of less than or equal to about 50 nm.

[0050] In certain embodiments, the surface smoothing process comprises a polishing step adapted to smooth one or both surfaces of the pressed shape to form an porous anode including a surface or surfaces having a smooth surface characterized by a surface roughness of less than or equal to about 100 nm and ion etching step applied to the smoothed surface or surfaces to open surface nanopores that may have been closed or plugged during the polishing step.

[0051] In certain embodiments, the polishing step comprises mechanical polishing. In other embodiments, the polishing step comprises chemical polishing. In other embodiments, the polishing

step comprises chemical-mechanical polishing (CMP).

[0052] In certain embodiments, the sintered slab has a thickness greater than or equal to about 3 mm. In other embodiments, the sintered slab has a thickness greater than or equal to about 4 mm. In other embodiments, the sintered slab has a thickness greater than or equal to about 5 mm.

[0053] In certain embodiments, the slices have thicknesses between about 1 mm and about 1 μm . In other embodiments, the slices have thicknesses between about 500 μm and about 1 μm . In other embodiments, the slices have thicknesses between about 250 μm and about 1 μm . In other embodiments, the slices have thicknesses between about 100 μm and about 1 μm . In other embodiments, the slices have thicknesses between about 50 μm and about 1 μm .

[0054] The cutting step includes, but is not limited to, string saw cutting, diamond blade cutting, spark cutting, laser cutting, mechanical cutting, or combinations thereof.

Anode Constructs

[0055] Embodiments of the present invention broadly relates to porous metal anode construct fabrication processes including mixing a metallic nanopowder and a proppant or pore forming nanopowder to form a nanopowder mixture, where the metallic nanopowder includes particles having particle sizes between about 10 nm and 1000 nm or 1 μm and the nanopowder proppant particles are adapted to keep the metallic nanopowder particles separated and to form pores in a resulting anode. The processes also include pressing the mixture under pressing conditions of pressing time, pressing temperature, and pressing pressure to form a pressed shape. The processes further include heating the pressed shape in an inert gas environment under heating conditions of heating time, heating temperature, and heating pressure sufficient to sinter the mixture and to decompose the proppant or pore forming particles in the pressed shape to form a metal anode composition having a porous surface and a porous interior, where the porous surface comprises nanopores having a size between about 10 nm and about 1000 nm or 1 μm . The processes further include depositing a thin film oxide electrolyte of the nanoporous processed surface of the metal anode composition yielding a continuous, impermeable thin film electrolyte layer having no or substantially no gas leakage through the electrolyte layer and permitting no or substantially no shorting of the anode to a cathode through the electrolyte layer. Of course, the constructs may be formed from the slabs or slices as set forth above.

[0056] In certain embodiments, prior to the depositing step, the processes may further include a surface smoothing process designed to further expose and define the surface nanopores and/or reduce surface roughness or improve surface smoothness.

[0057] In certain embodiments, the surface smoothing process comprises a polishing step adapted to smooth one or both surfaces of the pressed shape, the slab, or the slices to form a porous anode including a surface or surfaces having a smooth surface characterized by a surface roughness of less

than or equal to about 100 nm. In other embodiments, the smooth surface characterized by a surface roughness of less than or equal to about 50 nm.

[0058] In certain embodiments, surface smoothing process comprises a polishing step adapted to smooth one or both surfaces of the pressed shape, the slab, or the slices to form a porous anode including a surface or surfaces having a smooth surface characterized by a surface roughness of less than or equal to about 100 nm and ion etching step applied to the smoothed surface or surfaces to open surface nanopores that may have been closed or plugged during the polishing step.

[0059] In certain embodiments, the polishing step comprises mechanical polishing. In other embodiments, the polishing step comprises chemical polishing. In other embodiments, the polishing step comprises chemical-mechanical polishing (CMP).

SOFCs

[0060] Embodiments of the present invention broadly relates to SOFC and TFSOFC fabrication processes including mixing a metallic nanopowder and a proppant or pore forming nanopowder to form a nanopowder mixture, where the metallic nanopowder includes particles having particle sizes between about 10 nm and 1000 nm or 1 μm and the nanopowder proppant particles are adapted to keep the metallic nanopowder particles separated and to form pores in a resulting anode. The processes also include pressing the mixture under pressing conditions of pressing time, pressing temperature, and pressing pressure to form a pressed shape. The processes further include heating the pressed shape in an inert gas environment under heating conditions of heating time, heating temperature, and heating pressure sufficient to sinter the mixture and to decompose the proppant or pore forming particles in the pressed shape to form a metal anode composition having a porous surface and a porous interior, where the porous surface comprises nanopores having a size between about 10 nm and about 1000 nm or 1 μm . The processes further include depositing an electrolyte layer on a surface of the metal anode composition to form an anode construct, where the electrolyte layer is continuous and impermeable having no or substantially no gas leakage through the electrolyte layer and permitting no or substantially no shorting of the anode to a cathode through the electrolyte layer. The processes further include depositing a cathode on the electrolyte layer to form a SOFC of this invention. Of course, the constructs may be formed from the slabs or slices described above and herein.

TFSOFCs

[0061] Embodiments of the present invention broadly relates to SOFC and TFSOFC fabrication processes including mixing a metallic nanopowder and a proppant or pore forming nanopowder to form a nanopowder mixture, where the metallic nanopowder includes particles having particle sizes between about 10 nm and 1000 nm or 1 μm and the nanopowder proppant particles are adapted to

keep the metallic nanopowder particles separated and to form pores in a resulting anode. The processes also include pressing the mixture under pressing conditions of pressing time, pressing temperature, and pressing pressure to form a pressed shape. The processes further include heating the pressed shape in an inert gas environment under heating conditions of heating time, heating temperature, and heating pressure sufficient to sinter the mixture and to decompose the proppant or pore forming particles in the pressed shape to form a metal anode composition having a porous surface and a porous interior, where the porous surface comprises nanopores having a size between about 10 nm and about 1000 nm or 1 μm . The processes further include depositing a thin film of an oxide electrolyte on a surface of the metal anode to form a metal anode construct, where the thin film electrolyte layer is continuous and impermeable having no or substantially no gas leakage through the electrolyte layer and permitting no or substantially no shorting of the anode to a cathode through the electrolyte layer. The processes further include depositing a cathode on the electrolyte layer to form a SOFC of this invention. Of course, the constructs may be formed from the slabs or slices described above or herein. In certain embodiments, the electrolyte layer has a thickness of about 1 μm . In certain embodiments, the depositing steps comprise physical deposition, chemical vapor deposition, other thin film deposition processes, or mixtures and combinations thereof.

[0062] In certain embodiments, prior to the depositing step of the above SOFC and TFSOFC processes, the processes may further include a surface smoothing process designed to further expose and define the surface nanopores and/or reduce surface roughness or improve surface smoothness.

[0063] In certain embodiments, the surface smoothing process comprises a polishing step adapted to smooth one or both surfaces of the pressed shape, the slab, or the slices to form a porous anode including a surface or surfaces having a smooth surface characterized by a surface roughness of less than or equal to about 100 nm. In other embodiments, the smooth surface characterized by a surface roughness of less than or equal to about 50 nm.

[0064] In certain embodiments, surface smoothing process comprises a polishing step adapted to smooth one or both surfaces of the pressed shape, the slab, or the slices to form a porous anode including a surface or surfaces having a smooth surface characterized by a surface roughness of less than or equal to about 100 nm and ion etching step applied to the smoothed surface or surfaces to open surface nanopores that may have been closed or plugged during the polishing step.

[0065] In certain embodiments, the polishing step comprises mechanical polishing. In other embodiments, the polishing step comprises chemical polishing. In other embodiments, the polishing step comprises chemical-mechanical polishing (CMP).

Anodes, Anode Constructs, SOFCs, and TFSOFCs

Anode Precursor Compositions

[0066] Embodiments of this invention broadly relate to SOFC metal anode precursor compositions including a pressed shape comprising a nanopowder mixture including a metal nanopowder comprising particles having particle sizes between about 10 nm and 1000 nm or 1 μm and the proppant nanopowder comprising particles adapted to keep the metallic nanopowder particles separated.

Anodes

[0067] Embodiments of this invention broadly relate to SOFC porous anodes including a porous interior and a porous surface, where the surface and interior pores arise from decomposition of proppant or pore forming particles of an anode precursor composition including a pressed shape comprising a nanopowder mixture including a metal nanopowder comprising particles having particle sizes between about 10 nm and 1000 nm or 1 μm and the proppant nanopowder comprising particles adapted to keep the metallic nanopowder particles separated.

Anode Constructs

[0068] Embodiments of this invention broadly relate to solid oxide fuel cell (SOFC) porous anode constructs including an anode layer having a porous interior and a porous surface and an electrolyte layer formed on a surface of the anode layer, where the surface and interior pores arise from decomposition of proppant or pore forming particles of an anode precursor composition including a pressed shape comprising a nanopowder mixture including a metal nanopowder comprising particles having particle sizes between about 10 nm and 1000 nm or 1 μm and the proppant nanopowder comprising particles adapted to keep the metallic nanopowder particles separated and where the electrolyte layer is continuous and impermeable having no or substantially no gas leakage through the electrolyte layer and permitting no or substantially no shorting of the anode to a cathode through the electrolyte layer. In certain embodiments, the electrolytic layer is a continuous, dense, and electrically insulating thin film.

SOFCs

[0069] Embodiments of this invention broadly relate to SOFCs including a metal anode layer including a porous interior and a porous surface, an electrolyte layer formed on a surface of the metal, and a cathode layer formed on the electrolyte layer. The surface and interior pores arise from decomposition of proppant or pore forming particles of an anode precursor composition including a pressed shape comprising a nanopowder mixture including a metal nanopowder comprising particles having particle sizes between about 10 nm and 1000 nm or 1 μm and the proppant nanopowder comprising particles adapted to keep the metallic nanopowder particles separated. The electrolyte layer is continuous and impermeable having no or substantially no gas leakage through the electrolyte layer and permitting no or substantially no shorting of the anode to a cathode through the electrolyte

layer. In certain embodiments, the electrolytic layer is a continuous, dense, and electrically insulating thin film.

TFSOFCs

[0070] Embodiments of this invention broadly relate to SOFCs including a metal anode layer including a porous interior and a porous surface, an electrolyte layer formed on a surface of the metal, and a cathode layer formed on the electrolyte layer. The surface and interior pores arise from decomposition of proppant or pore forming particles of an anode precursor composition including a pressed shape comprising a nanopowder mixture including a metal nanopowder comprising particles having particle sizes between about 10 nm and 1000 nm or 1 μ m and the proppant nanopowder comprising particles adapted to keep the metallic nanopowder particles separated. The electrolyte layer is continuous and impermeable having no or substantially no gas leakage through the electrolyte layer and permitting no or substantially no shorting of the anode to a cathode through the electrolyte layer. In certain embodiments, the electrolytic layer is a continuous, dense, and electrically insulating thin film.

[0071] In certain embodiments of the above anodes, anode constructs, SOFCs, or TFSOFCs, the surface pores have pore sizes between about 10 nm and about 1000 nm, the interior pores have pore sizes between about 10 nm and about 10 microns, and the surface has a roughness of less than or equal to about 100 nm. In other embodiments, the surface pores have pore sizes between about 10 nm and about 500 nm, the interior pores have pore sizes between about 10 nm and about 10 microns, and the surface has a roughness of less than or equal to about 50 nm.

[0072] In certain embodiments, the metal anode comprises nickel, gold, platinum, or mixtures and combinations thereof. In other embodiments, the anode comprises nickel. In other embodiments, the anode comprises gold. In other embodiments, the anode comprises platinum.

[0073] In certain embodiments, the metal anode is comprised of a metallic component and a ceramic or nonmetallic component. In other embodiments, the metallic component comprises nickel, gold, platinum, or mixtures and combinations thereof and the ceramic or nonmetallic component comprise cermets, ceramic mixtures, or mixtures and combinations thereof. In other embodiments, the cermets and ceramics comprise metal oxides, metal borides, metal carbides, or mixtures and combinations thereof. In other embodiments, the cermet or ceramic is yttria stabilized zirconia (YSZ).

SUITABLE REAGENTS AND COMPONENTS OF THE INVENTION

[0074] Suitable metallic agents or metal containing materials for use in the invention include, without limitation, a nickel containing material, a gold containing material, a platinum containing material, a molybdenum containing material, a cobalt containing material, or mixtures and combinations thereof. Exemplary examples of metal containing materials include, without limitation, metals, metal-

cermets, metal-ceramic mixtures, or mixtures and combinations thereof. Exemplary metals include, without limitation, nickel, cobalt, molybdenum, gold, platinum, or mixtures and combinations thereof. Exemplary examples of metal-cermets include, without limitation, nickel-cermets, molybdenum-cermets, cobalt-cermets, or mixtures thereof. Cermets are mixtures of the metals and ceramics. Exemplary examples of the ceramics include, without limitation, metal oxides, metal borides, metal carbides, or mixtures and combinations thereof. In certain embodiments, the metal oxides comprises yttria stabilized zirconia (YSZ). In certain embodiments, the metal-cermet comprises nickel-YSZ cermet.

[0075] Suitable proppants or pore forming agents for use in the invention include, without limitation, hydrogen peroxide, ammonium bicarbonate, ammonium hydroxide, organic peroxides, organic hydroperoxides, fused ring aromatics, ammonium carboxylates, or mixtures and combinations thereof. Exemplary organic peroxides include, without limitation, methyl ethyl ketone peroxide, methyl isobutyl ketone peroxide, benzoyl peroxide, acetyl benzoyl peroxide, di-(1-naphthoyl)peroxide, or mixtures and combinations thereof. Exemplary organic hydroperoxides include, without limitation, ethyl hydroperoxide, t-butyl hydroperoxide, or mixtures and combinations thereof. Exemplary fused ring aromatics include, naphthalene, anthracene, benzofuran, isobenzofuran, or mixtures and combinations thereof. Exemplary examples of ammonium carboxylates include, without limitation, ammonium formate, ammonium acetate, ammonium propionate, higher ammonium carboxylates, or mixtures and combinations thereof. Proppant powders that may be used in this processes of this invention include, without limitation, any nanopowder material that is non-reactive or substantially non-reactive with metals of the metallic agents and may be removed or decomposed at temperatures in a range between about 40°C to about 400°C. Further, the addition of a catalyst may also be appropriate such as sugars or polyols including, without limitation, sucrose, fructose, glucose, sorbitol, or mixtures and combination thereof. The proppant removal may be via evaporation, sublimation, or any other physical process that cause some or all of the proppant to be removed from the mixture during subsequent processing.

DETAILED DESCRIPTION OF THE DRAWINGS

Anode Structure

[0076] Referring now to **Figure 1A**, a metallic anode of this invention, generally **100**, is shown to include macro-pores **102** in the bulk material **104** and nanopores **106** at its surface **108**.

[0077] Referring now to **Figure 1B**, a metallic anode construct of this invention, generally **120**, is shown to include a metallic anode layer **122** including macro-pores **124** in the bulk material **126** and nanopores **128** at its surface **130**. The construct **120** also includes an electrolyte layer **132** deposited on the surface **130** of the anode layer **122**.

[0078] Referring now to **Figure 1C**, an SOFC or TFSOFC of this invention, generally **160**, is shown to include a metallic anode layer **162** including macro-pores **164** in the bulk material **166** and nanopores **168** at its surface **170**. The SOFC or TFSOFC **160** also includes an electrolyte layer **172** deposited on the surface **170** of the anode layer **162**. The SOFC or TFSOFC **160** also includes a cathode layer **174** deposited on a surface **176** of the electrolyte layer **172**.

Methods for Making Anodes, Anode Constructs, SOFCs and TFSOFCs

[0079] Referring now to **Figure 2A**, an embodiment of a flow diagram of a fabrication process for making porous metal anodes of this invention, generally **200**, is shown to include a mixing step **202**, where the mixing step **202** comprises mixing (a) a metallic or metal nanopowder or a plurality of metallic or metal nanopowders and (b) a proppant a pore forming agent nanopowder or a plurality of proppants or pore forming agent nanopowders to form a nanopowder mixture, where the metallic or metal particles having a particle size between about 10 nm and about 1000 nm (1 μ m) and the proppants or pore forming particles having a particle size between about 10 nm and about 500 nm. The process **200** also includes a pressing step **204**, where the pressing step **204** comprises pressing the nanopowder mixture under pressing conditions including a pressing time, a pressing temperature and a pressing pressure sufficient to form a pressed shape having a desired thickness. The process **200** also includes a sintering step **206**, where the sintering step **206** comprises heating the pressed shape in an inert gas environment (*e.g.*, a hydrogen gas environment) under heating conditions including a heat time, a heating temperature, and a heating pressure sufficient to sinter the metallic particles in the mixture and to decompose the proppant(s) or pore forming agent(s) to form an SOFC or TFSOFC anode.

[0080] Referring now to **Figure 2B**, another embodiment of the flow diagram of the fabrication process for making porous metal anodes **200** is shown to further include a polishing step **208**, where the polishing step **208** comprises polishing a top surface or a top surface and bottom surface of the SOFC anode or an TFSOFC anode to form a smoothed surface SOFC or TFSOFC anode.

[0081] Referring now to **Figure 2C**, another embodiment of the flow diagram of the fabrication process for making porous metal anodes **200** is shown to further include an etching step **210**, where the etching step **210** comprises ion etching the smoothed surface or surfaces of the smoothed surface SOFC anode to form an ion etched, smoothed surface SOFC or TFSOFC anode.

[0082] Referring now to **Figure 3A**, an embodiment of a flow diagram of another fabrication process for making porous metal anodes of this invention, generally **300**, is shown to include a mixing step **302**, where the mixing step **302** comprises mechanically mixing (a) a nanopowder metallic agent or a plurality of nanopowder metallic agents and (b) a nanopowder proppant or pore forming agent or a plurality of nanopowder proppants or pore forming agents to form a nanopowder mixture, where

the nanopowder metallic agent or agents comprise particles having particle sizes between about 10 nm and about 500 nm and the nano proppant or proppants or pore forming agent or agents comprise particles having particle sizes between about 10 nm and about 500 nm. The process **300** also includes a pressing step **304**, where the pressing step **304** comprises pressing the nanopowder mixture under pressing conditions including a pressing time, a pressing temperature and a pressing pressure sufficient to form a pressed shape having a desired thickness. The process **300** also includes a sintering step **306**, where the sintering step **306** comprises heating the pressed shape in an inert gas environment (*e.g.*, a hydrogen gas environment) under heating conditions including a heat time, a heating temperature, and a heating pressure sufficient to sinter the metallic particles in the mixture and to decompose the proppant(s) or pore forming agent(s) to form an SOFC or TFSOFC anode sufficient to sinter the metallic particles in the mixture and to decompose the pore forming agent(s) in the mixture to form an anode composition comprising a sintered slab. The process **300** also includes a slicing step **308**, where the slicing step **308** comprise slicing the sintered slab into slices having a desired thickness.

[0083] Referring now to **Figure 3B**, another embodiment of the flow diagram of the fabrication process for making porous metal anodes **300** is shown to further include a polishing step **310** for polishing the slices, where the polishing step **310** comprises mechanically polishing a top surface or a top surface and a bottom surface of each slice to form an anode composition including at least one smoothed surface.

[0084] Referring now to **Figure 3C**, another embodiment of the flow diagram of the fabrication process for making porous metal anodes **300** is shown to further include an etching step **312**, where the etching step **312** comprises ion etching the smoothed surface or surfaces to form an anode composition including at least one ion etched and smoothed surface.

EXPERIMENTS OF THE INVENTION

[0085] The porous metal anode is fabricated by mixing a metallic nanopowder *e.g.*, nickel-cermet nanopowder and a proppant nanopowder to form a metal nanopowder/proppant nanopowder mixture. In certain embodiments, the mixing of the two components is thorough. The mixing may comprise a mechanical mixing procedure such as for example a ball milling procedure, a cryogenic grinding procedure, or a mixture of these procedures. The mixture is then pressed in a press at a temperature and a pressure sufficient to form a shape such as a round disc, a square, or other desired shape, where the temperature ranges from room temperature or an elevated temperature and the pressure ranges between about 100 psi and about 10,000 psi. In certain embodiments, the pressure ranges between about 1,000 psi and about 10,000 psi. In other embodiments, the pressure ranges between about 5,000 psi and about 10,000 psi. In other embodiments, the pressure is about 10,000 psi. In certain

embodiments, the elevated temperature is a moderate temperature between about 20°C and about 100°C. In certain embodiments, a thickness of the shape is between about 10 cm and about 1 μm. In certain embodiments, the thickness is between about 1 mm and about 10 μm. In other embodiments, the thickness is between about 0.1 mm (100 μm) and about 10 μm. In certain embodiments, a die used for pressing the mixture includes parallel top and bottom sections so that the shape (*e.g.*, disc) of the metal powder/proppant mixture has parallel or substantially parallel top and bottom surfaces. In other embodiments, the die faces are sufficiently smooth so that the shape has at least one smooth surface. In certain embodiments, each smooth surface characterized by having small surface pores and a high surface smoothness. Smooth surfaces are important for the formation or deposition of a continuous and dense electrolyte thin film layer on top of the surfaces of the shape to form an anode composition of this invention including an anode layer covered with a dense electrolyte layer.

[0086] After the metal powder/proppant mixture is pressed into a shape, the shape is loaded into a furnace. In certain embodiments, the furnace is a controlled temperature and atmosphere furnace such as a tube furnace. The shape may be supported inside of the furnace so that at least one side of the shape is uncovered. In certain embodiments, a temperature of the furnace comprises an elevated temperature. In other embodiments, the elevated temperature in the oven/furnace is uniform or substantially uniform (within $\pm 5^\circ\text{C}$) so that the shape is uniformly or substantially uniformly heated achieving a uniform or substantially uniform temperature throughout the shape. A flow of non-oxidizing gas is maintained around the sample during heating at the elevated temperature. The gas environment comprises an inert gas, hydrogen gas, a hydrogen-inert gas mixture, nitrogen gas, or any other gas or gas mixture that is non-oxidizing to the metal component of the shape. In certain embodiments, the environment comprises a vacuum environment having a desired reduced pressure or vacuum level for non-oxidation of the metal component of the shape during the heating process. In other embodiments, the heating occurs for a time sufficient to sinter the mixture of the shape to form a sintered shape. In certain embodiments, a gas flow through the furnace may be controlled to be from a few standard cubic centimeters per minute (sccm) to several hundred sccm or between about 1 sccm to about 500 sccm. In other embodiments, the gas flow is between about 1 sccm and about 300 sccm. In other embodiments, the gas flow is between about 1 sccm and about 200 sccm. In other embodiments, the gas flow is between about 1 sccm and about 100 sccm. The shaped sample is heated in the furnace with an appropriate non-oxidizing atmosphere. In certain embodiments, the heating process starts at room temperature and is ramped up at a heating rate between about 1°C and about 20°C per minute up to an elevated temperature. In certain embodiments, the elevated temperature is between about 100°C and about 1000°C. In other embodiments, the elevated

temperature is between about 500°C and about 1000°C. In certain embodiments, the heating is continued for a period ranging between about 30 minutes and about ten hours under the controlled gas flow rate of the non-oxidizing gas. During the heating time, the shaped sample may shrink in size. After heating for the desired time and temperature, the shaped sample is cooled at a cooling rate between about 1°C and about 30°C per minute to room temperature.

[0087] After pressing and sintering, surfaces of either the a processed thin anode sample, or a thin sliced slab from a thick processed sample is nominally microscopically rough, although with pores of the appropriate few hundred nm in size as shown in **Figure 4A**. Such a surface, although it has the appropriate pore structure, is much too rough to be effectively uniformly and continuously coated with a thin film electrolyte layer. Hence, an additional processing step may be required to smooth one or both of the porous surfaces of the disc and still maintain nano-porosity. This additional step may be achieved as example by mechanically polishing the porous metal disc surface(s) using a number of different polishing pastes, which may include both different composition polishing pastes as well as different particle size polishing pastes. These pastes may include diamond paste, aluminum oxide paste, silicon carbide paste, tungsten carbide paste, any number of other polishing paste compositions of the above or other hard materials or mixtures and combinations thereof. The particle size of the hard materials in the polishing pastes may vary from as large as from about 50 μ to about 100 nm. In certain embodiments, the particle size is from about 10 μ to about 100 nm. The porous metal disc is polished smooth to a roughness is less than or equal to about 50 nm as shown **Figure 4B**. In other embodiments, the roughness of the polished smooth surface is less than or equal to about 40 nm. In other embodiments, the roughness of the polished smooth surface is less than or equal to about 30 nm. Chemical polishing or chemical mechanical polishing (CMP) may also be used to smooth the surface of the porous metal disc with monitoring the process to minimize etching and enlargement of the surface pores. Such polishing steps, especially mechanical polishing, may leave the surface pores somewhat closed due to metal fold-over into the surface pores. This effect can be mitigated by a final process step that will open the surface pores. Sonication may be used to remove the any polishing powder residue on/in the disc surface. The surface can then be chemically etched by appropriate acid etching for smoothing, or mechanical removal of material by inert gas ion bombardment can be applied to the porous nickel metal sample to open surface nanopores. The ion bombardment or ion etching is best done at an oblique angle to the surface which allows for more effective opening of closed pores and yet retains a relatively smooth surface. Nominal ion etch conditions include ion currents of from 5 mA/cm² to 50 mA/cm² at bias voltages of from 300 V to up to 1500 V. After ion etching, the finished product porous metal anode with nanoporous surface structure is shown in **Figure 4C**.

[0088] After ion etching or other surface nanopore opening process, the interior of the porous metal anode still retains large pores as shown in **Figure 5**, which better accommodate good gas flow through the anode. A porous metal anode with appropriate surface nanoporosity will allow for the deposition of a continuous and dense thin film electrolyte on the anode. This deposition of an electrolyte film of from 0.1 micron to 5 micron thickness can be accomplished by any number of physical or chemical vapor deposition processes including direct chemical deposition processes such as sol gel deposition. An example of a yttria stabilized zirconia (YSZ) film deposited by metal organic chemical vapor deposition (MOCVD) onto a complete processed porous nickel anode with nanoporous surface structure is shown in **Figure 6**. The complete coating of the porous metal surface with the YSZ layer should be noted along with the absence of any porosity in YSZ layer. The foregoing disclosure and description are illustrative and explanatory thereof, and various changes in the details of the method and apparatus can be made without departing from the spirit of the invention.

[0089] All references cited herein are incorporated by reference. Although the invention has been disclosed with reference to its preferred embodiments, from reading this description those of skill in the art may appreciate changes and modification that may be made which do not depart from the scope and spirit of the invention as described above and claimed hereafter.

CLAIMS

We claim:

1. A solid oxide fuel cell (SOFC) porous metal anode comprising:
a porous interior, and
a porous surface.
2. The anode of claim 1, wherein:
the surface pores have pore sizes between about 10 nm and about 1000 nm,
the interior pores have pore sizes between about 10 nm and about 10 microns,
the surface has a roughness of less than or equal to about 50 nm, and
the metal comprises nickel, gold, platinum, or mixtures and combinations thereof or the anode comprises a metallic component and a ceramic or nonmetallic component.
3. The anode of claim 2, wherein the metal comprises nickel, gold or platinum, the metallic component comprises nickel, gold, platinum, or mixtures and combinations thereof and the ceramic or nonmetallic component comprise cermets, ceramic mixtures, or mixtures and combinations thereof.
4. The composition of claim 3, wherein the cermets and ceramics comprise metal oxides, metal borides, metal carbides, or mixtures and combinations thereof.
5. The composition of claim 4, wherein the cermet or ceramic is yttria stabilized zirconia (YSZ).
6. A solid oxide fuel cell (SOFC) porous anode construct comprising:
a metal anode layer including a porous interior and a porous surface, and
an electrolytic layer formed on the porous surface,
where the electrolytic layer is a continuous, dense, and electrically insulating thin film.
7. The construct of claim 6, wherein:
the surface pores have pore sizes between about 10 nm and about 1000 nm,
the interior pores have pore sizes between about 10 nm and about 10 microns,
the surface has a roughness of less than or equal to about 50 nm, and
the metal of the metal anode comprises nickel, gold, platinum, or mixtures and combinations thereof or the anode is comprised of a metallic component and a ceramic or nonmetallic component.
8. The construct of claim 7, wherein the metal comprises nickel, gold or platinum or the metallic

component comprises nickel, gold, platinum, or mixtures and combinations thereof and the ceramic or nonmetallic component comprise cermets, ceramic mixtures, or mixtures and combinations thereof.

9. The composition of Claim 8, wherein the cermets and ceramics comprise metal oxides, metal borides, metal carbides, or mixtures and combinations thereof.

10. The composition of Claim 9, wherein the cermet or ceramic is yttria stabilized zirconia (YSZ).

11. A solid oxide fuel cell (SOFC) electrical construct comprising:
a metal anode layer including a porous interior and a porous surface,
an electrolytic layer formed on the porous surface, and
a metal cathode layer formed on the electrolytic layer,
where the electrolytic layer is a continuous, dense, and electrically insulating thin film eliminating shorting and eliminating gas flow through the construct.

12. The construct of claim 11, wherein:
the surface pores have pore sizes between about 10 nm and about 1000 nm,
the interior pores have pore sizes between about 10 nm and about 10 microns,
the surface has a roughness of less than or equal to about 50 nm, and
the metal of the metal anode comprises nickel, gold, platinum, or mixtures and combinations thereof or the anode is comprised of a metallic component and a ceramic or nonmetallic component.

13. The construct of claim 12, wherein the metal comprises nickel, gold or platinum or the metallic component comprises nickel, gold, platinum, or mixtures and combinations thereof and the ceramic or nonmetallic component comprise cermets, ceramic mixtures, or mixtures and combinations thereof.

14. The composition of Claim 13, wherein the cermets and ceramics comprise metal oxides, metal borides, metal carbides, or mixtures and combinations thereof.

15. The composition of Claim 14, wherein the cermet or ceramic is yttria stabilized zirconia (YSZ).

16. A method comprising the step:
combining a metallic nanopowder and a proppant nanopowder to form a nanopowder mixture,

pressing the nanopowder mixture into a pressed shape having a least one flat surface, and heating the pressed shape at an elevated temperature to form a sintered slab.

17. The method of Claim 14, further comprising:
polishing the flat surface of the sintered slab to a smooth surface having a roughness of less than or equal to about 50 nm.
18. The method of Claim 17, wherein the polishing step comprises mechanical polishing.
19. The method of Claim 17, wherein the polishing step comprises chemical polishing.
20. The method of Claim 17, wherein the polishing step comprises chemical-mechanical polishing (CMP).
21. The method of Claim 17, further comprising:
an additional step of pore opening to improve the opening of surface nanopores having a largest dimension of between about 10 nm and about 1000 nm
22. The method of Claim 21, wherein the additional step comprises ion etching, chemical etching or other technique for opening surface nanopores.
23. The method of Claim 13, further comprising:
depositing onto the smoothed surface an oxide electrolyte to form a continuous, dense, and electrically insulating thin film layer thereon.
24. The method of Claim 23, wherein the depositing step comprises physical deposition, chemical vapor deposition, other thin film deposition process or mixtures and combinations thereof.
25. The method of Claim 13, further comprising the step of:
after the depositing step, depositing a cathode layer on the insulating thin film layer to form a thin film solid oxide fuel cell electrical element.
26. The method of Claim 25, wherein the metallic nanopowder comprises particles having particle sizes between about 10 nm and 500 nm and the proppant nanopowder comprises particles having sizes between from 10 nm and 500 nm.

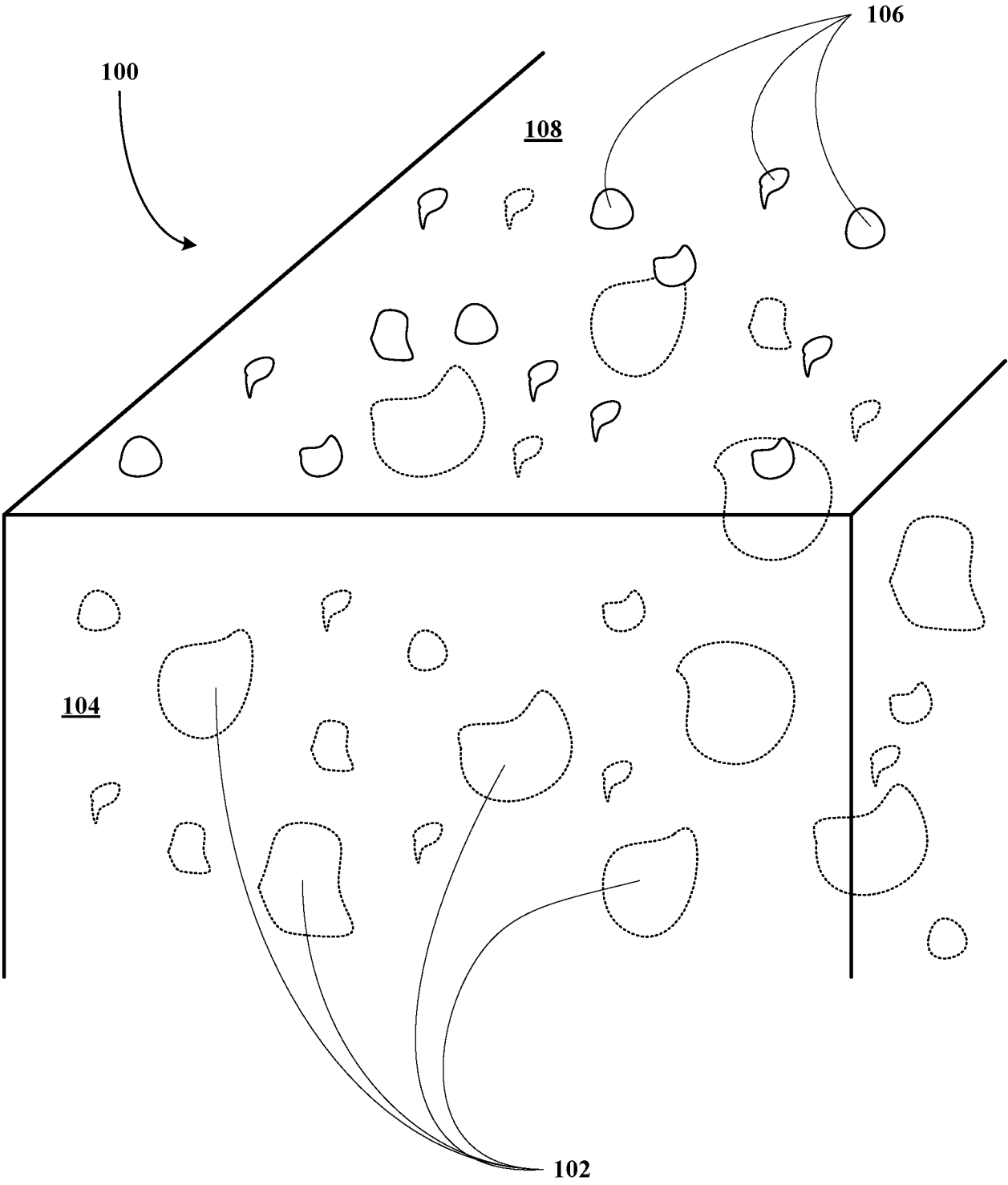


FIG. 1A

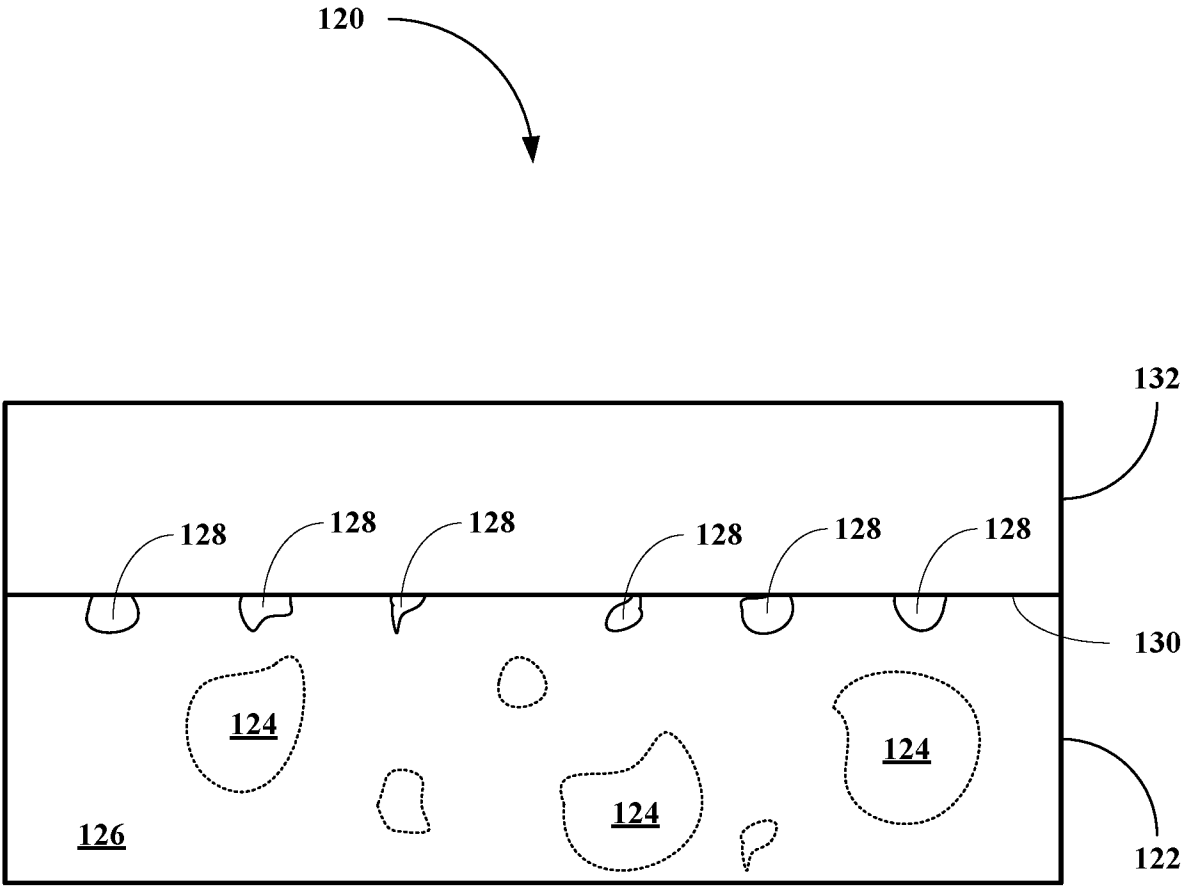


FIG. 1B

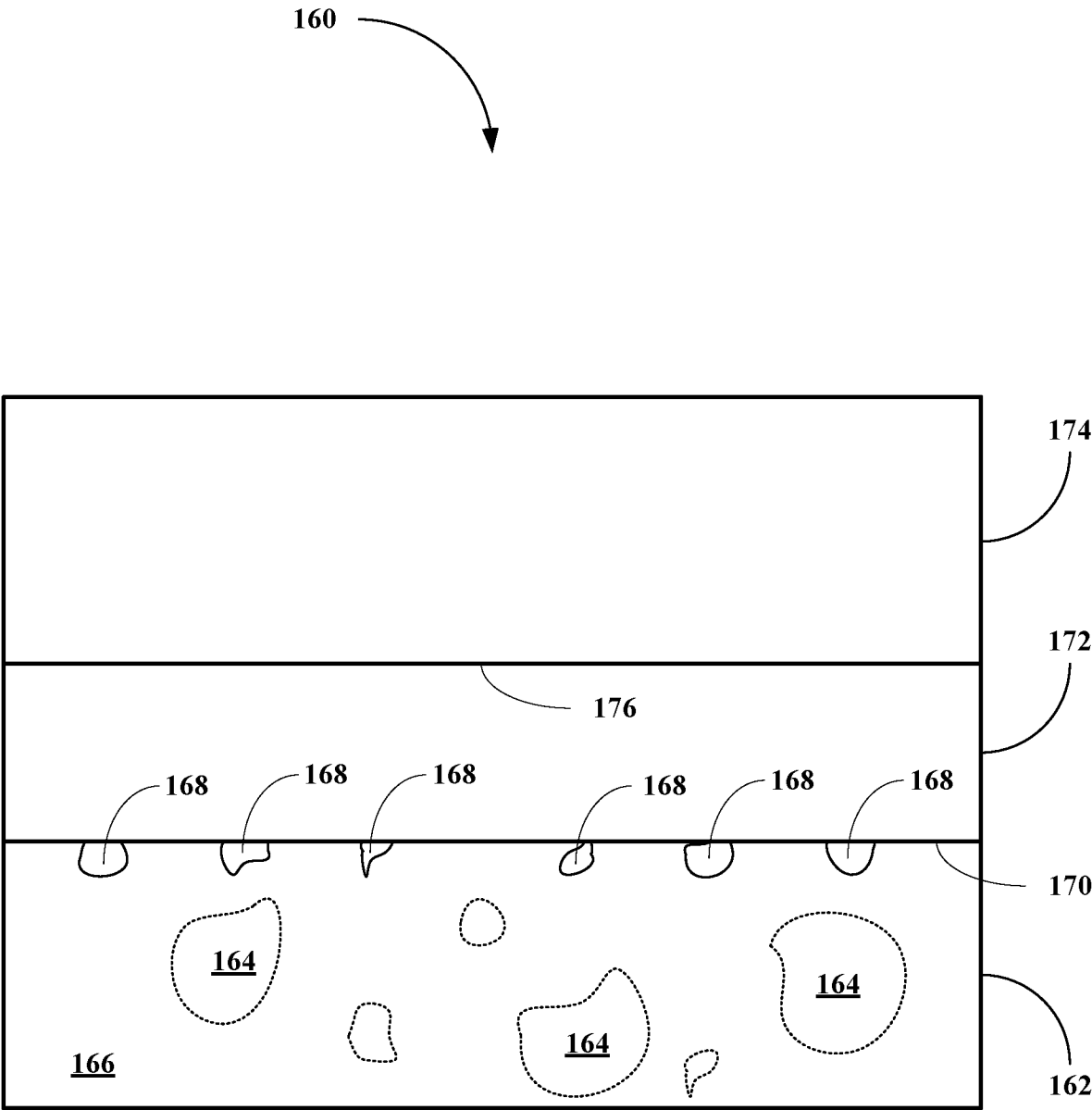
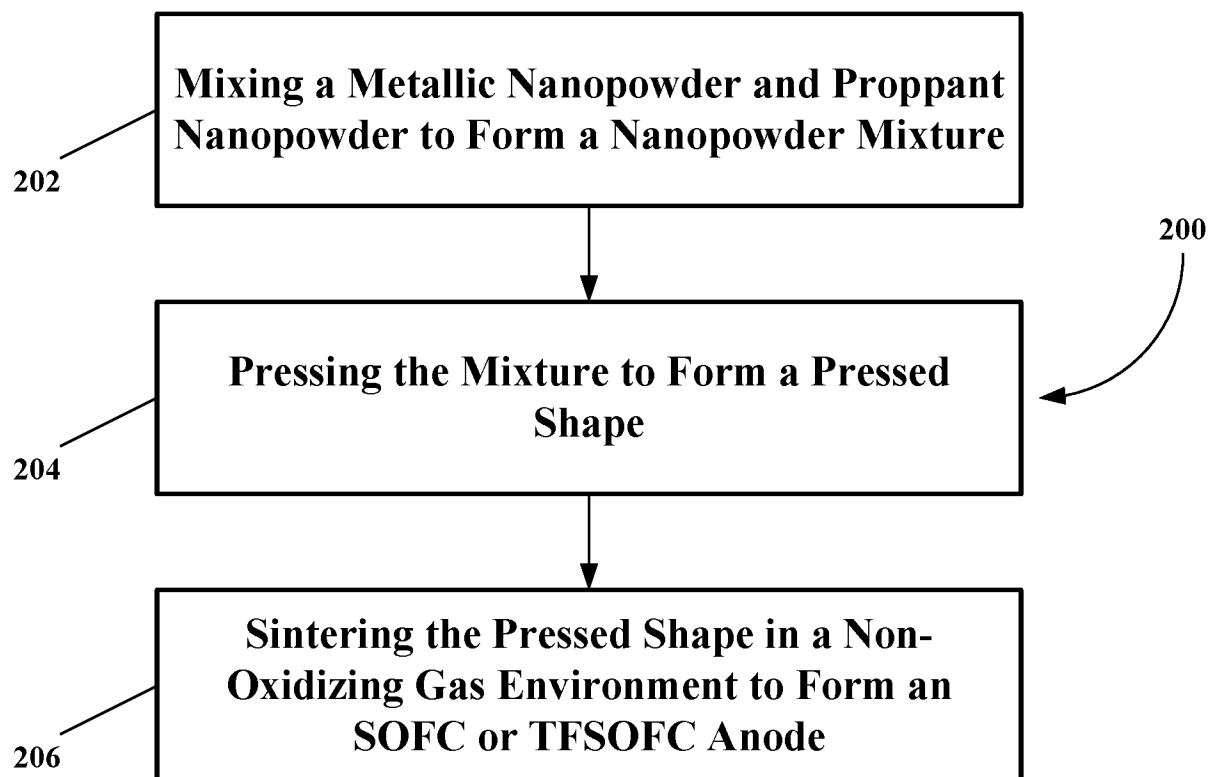
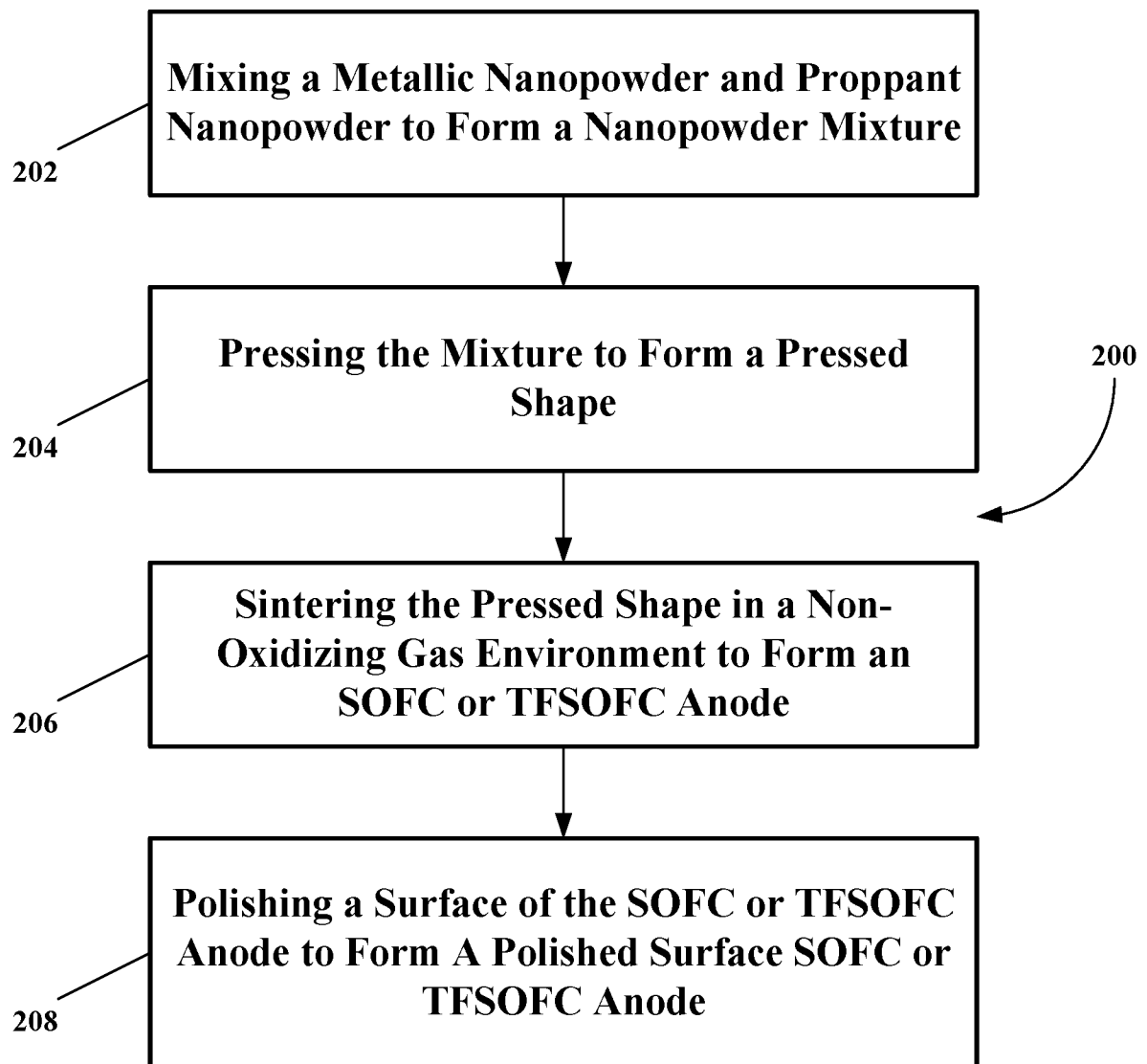


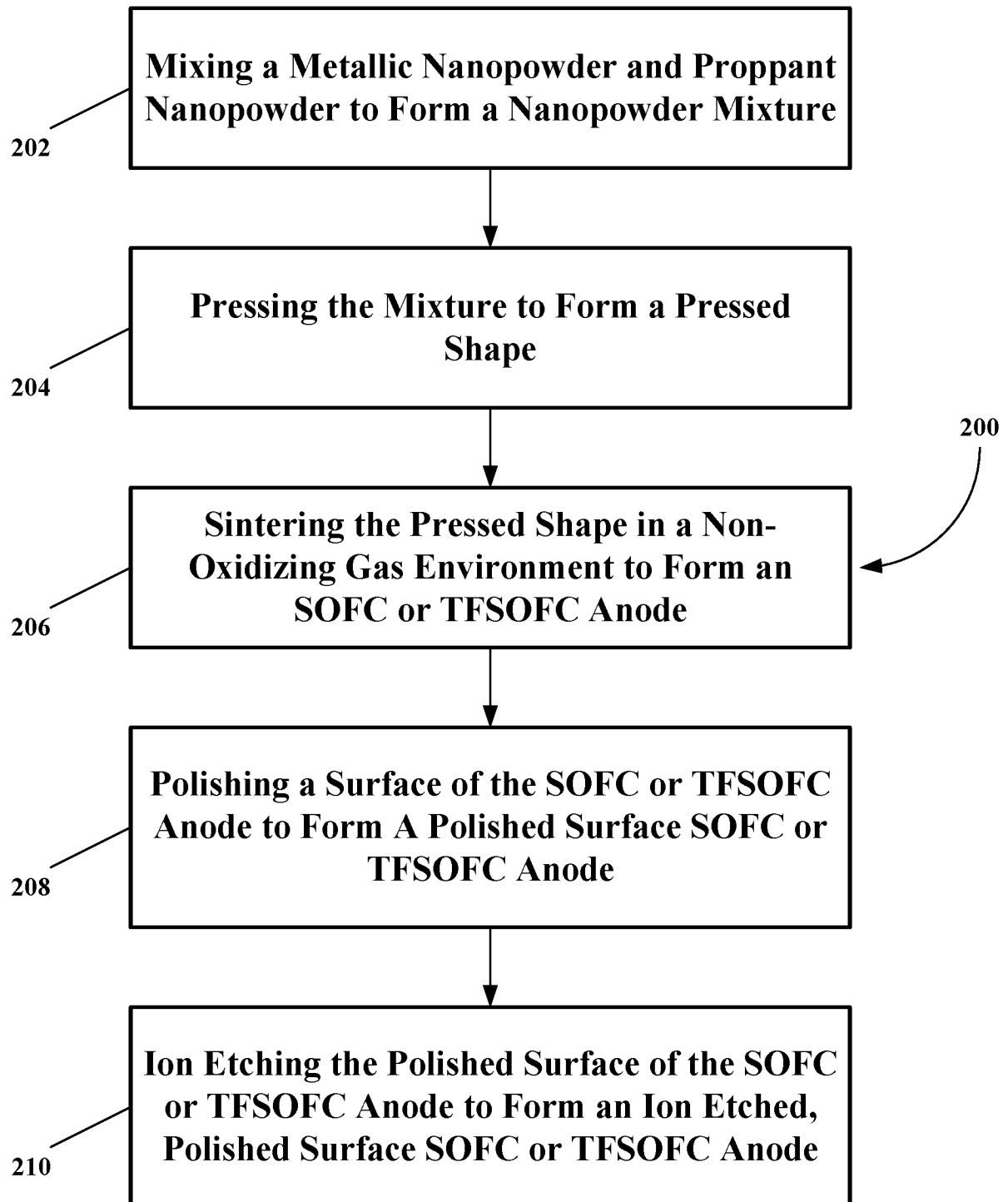
FIG. 1C

**FIG. 2A**

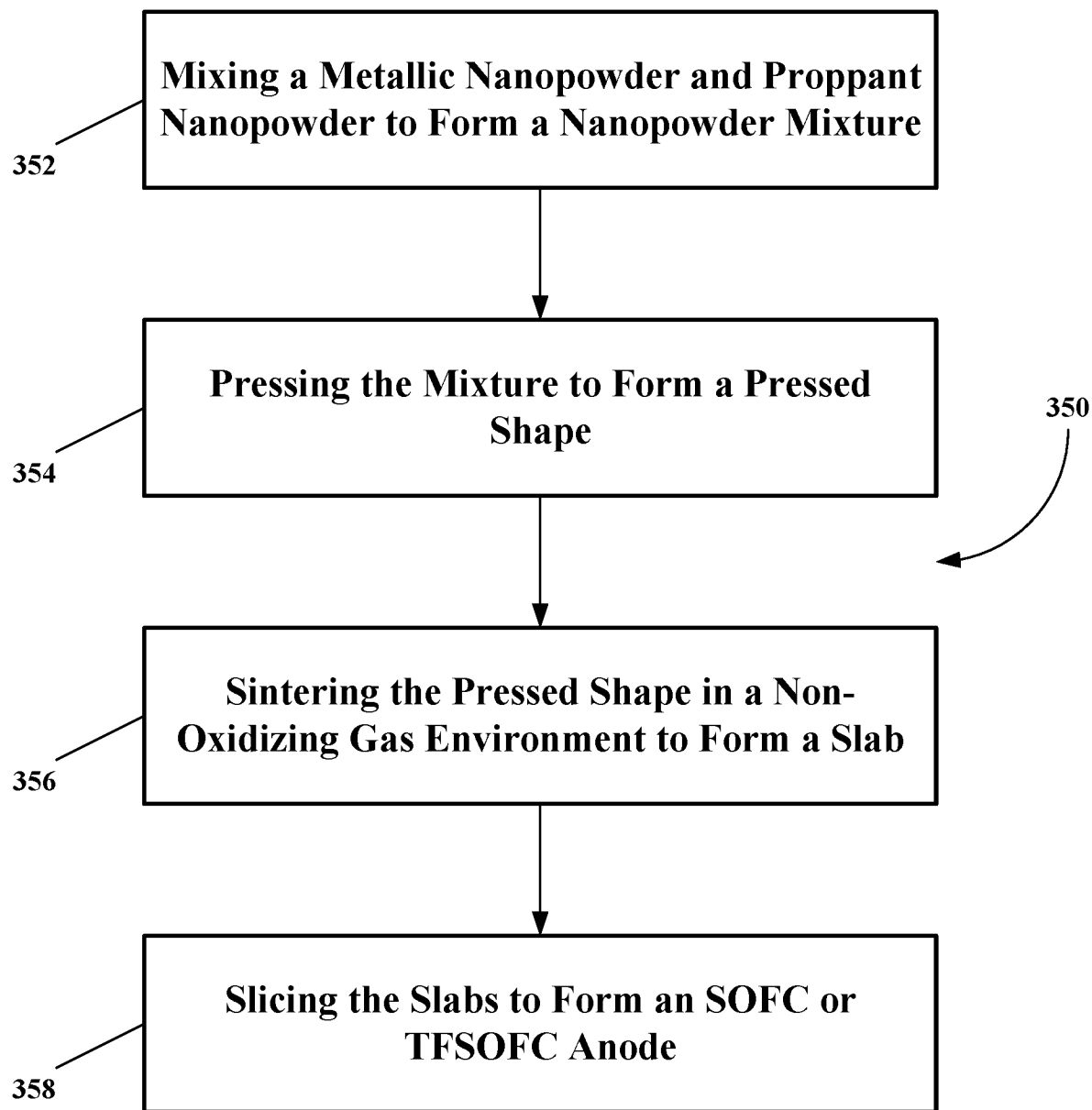
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**FIG. 2B**

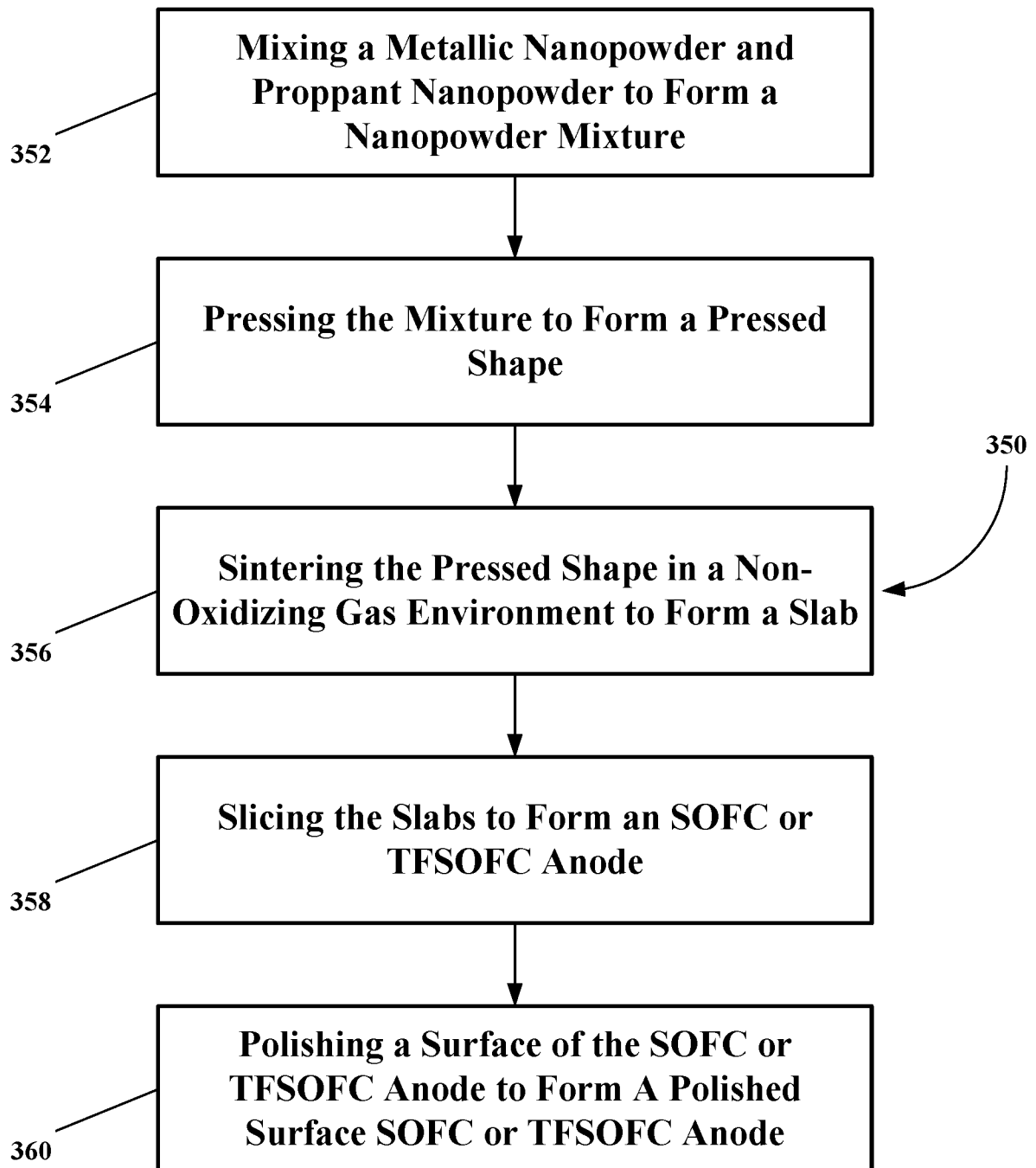
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**FIG. 2C**

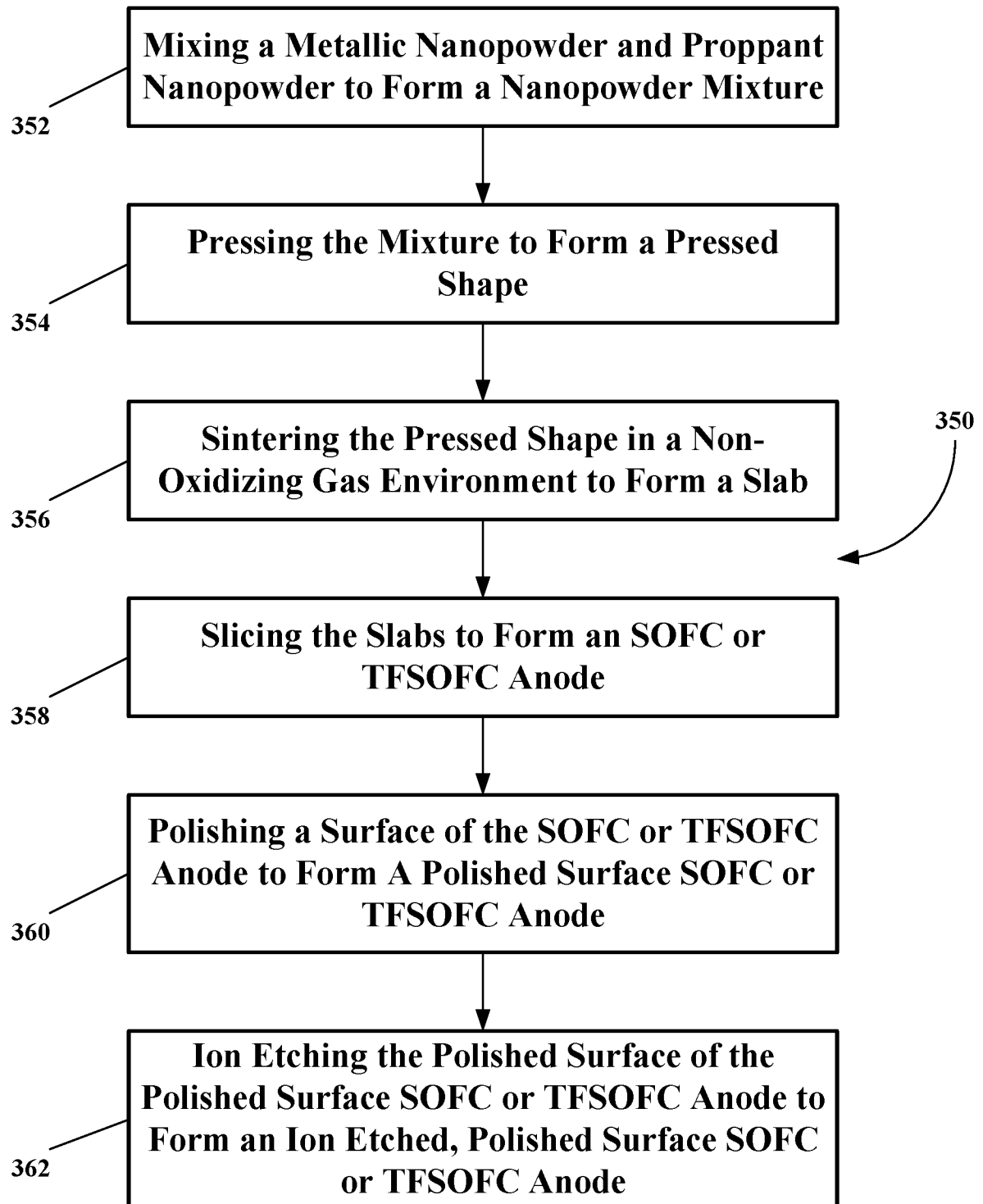
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**FIG. 3A**

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**FIG. 3B**

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**FIG. 3C**

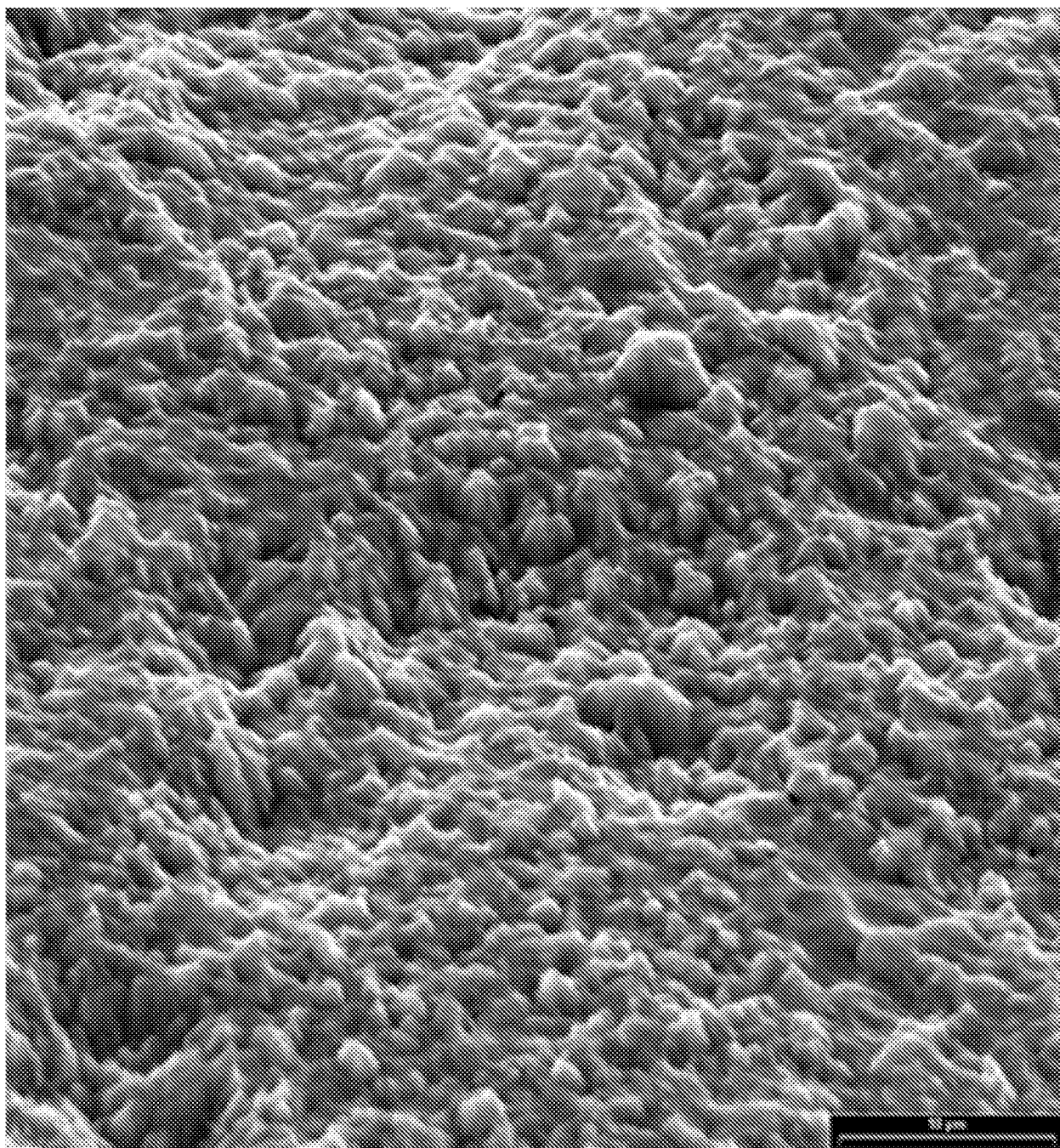


FIG. 4A

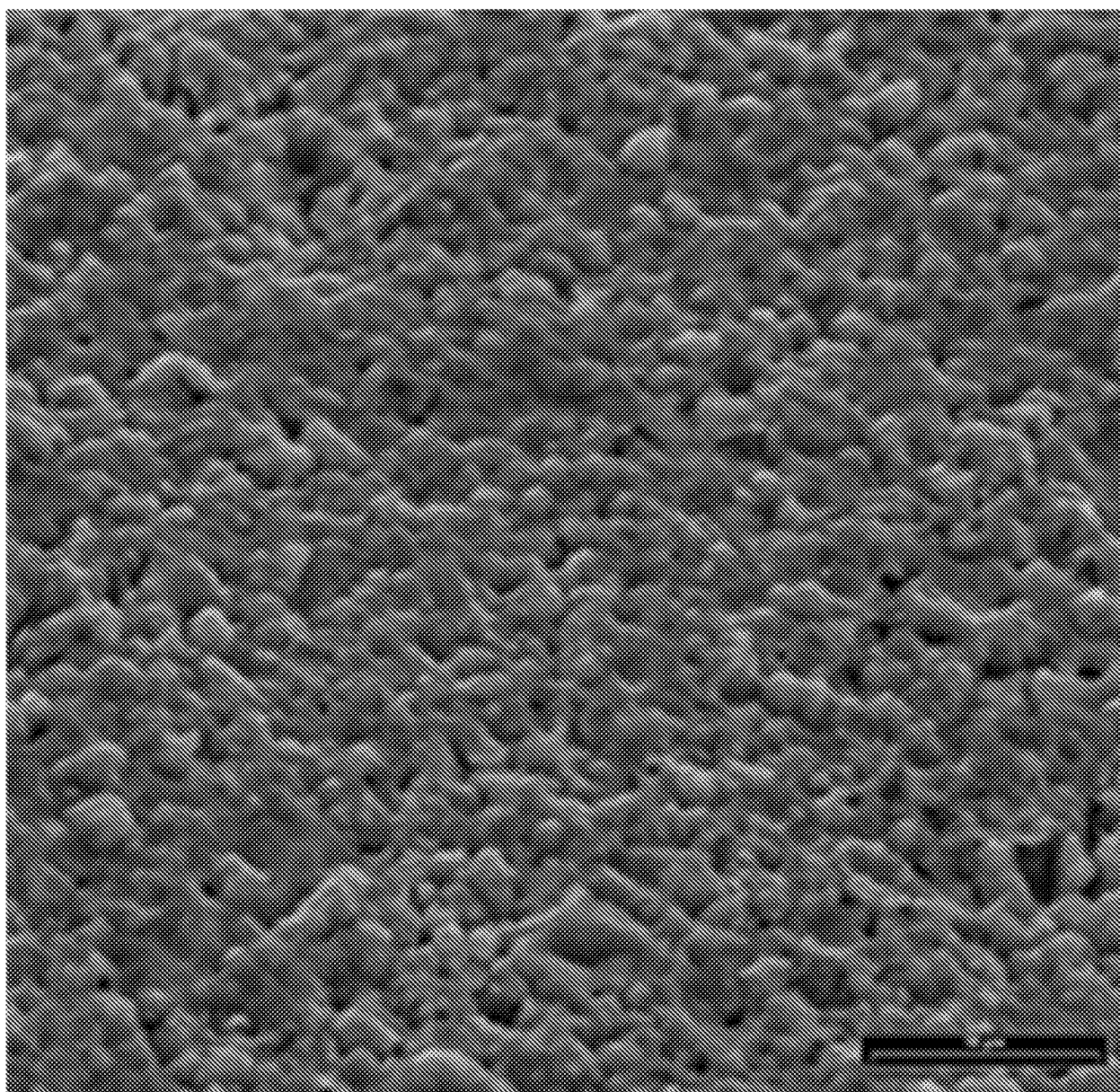


FIG. 4B

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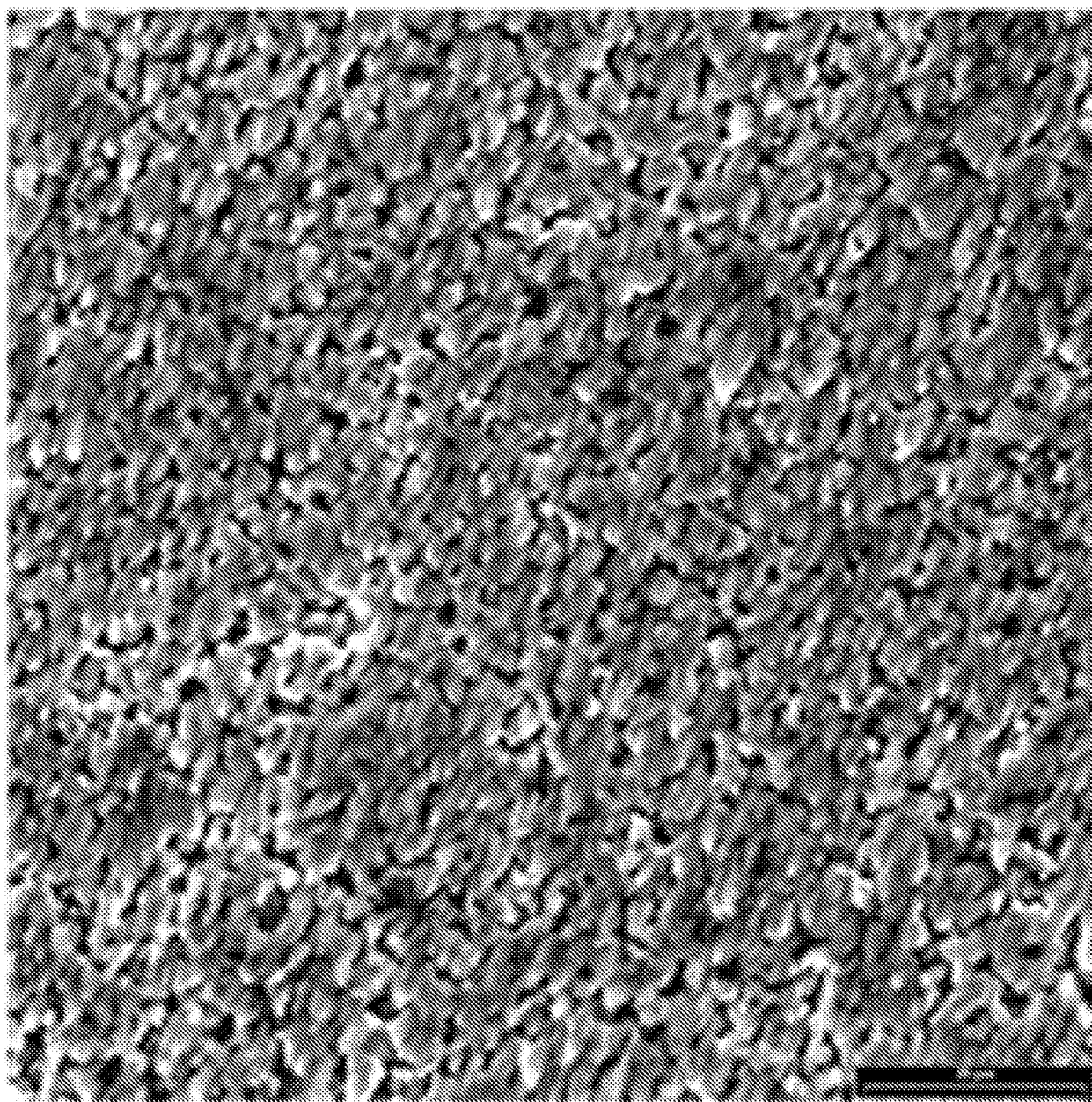


FIG. 4C

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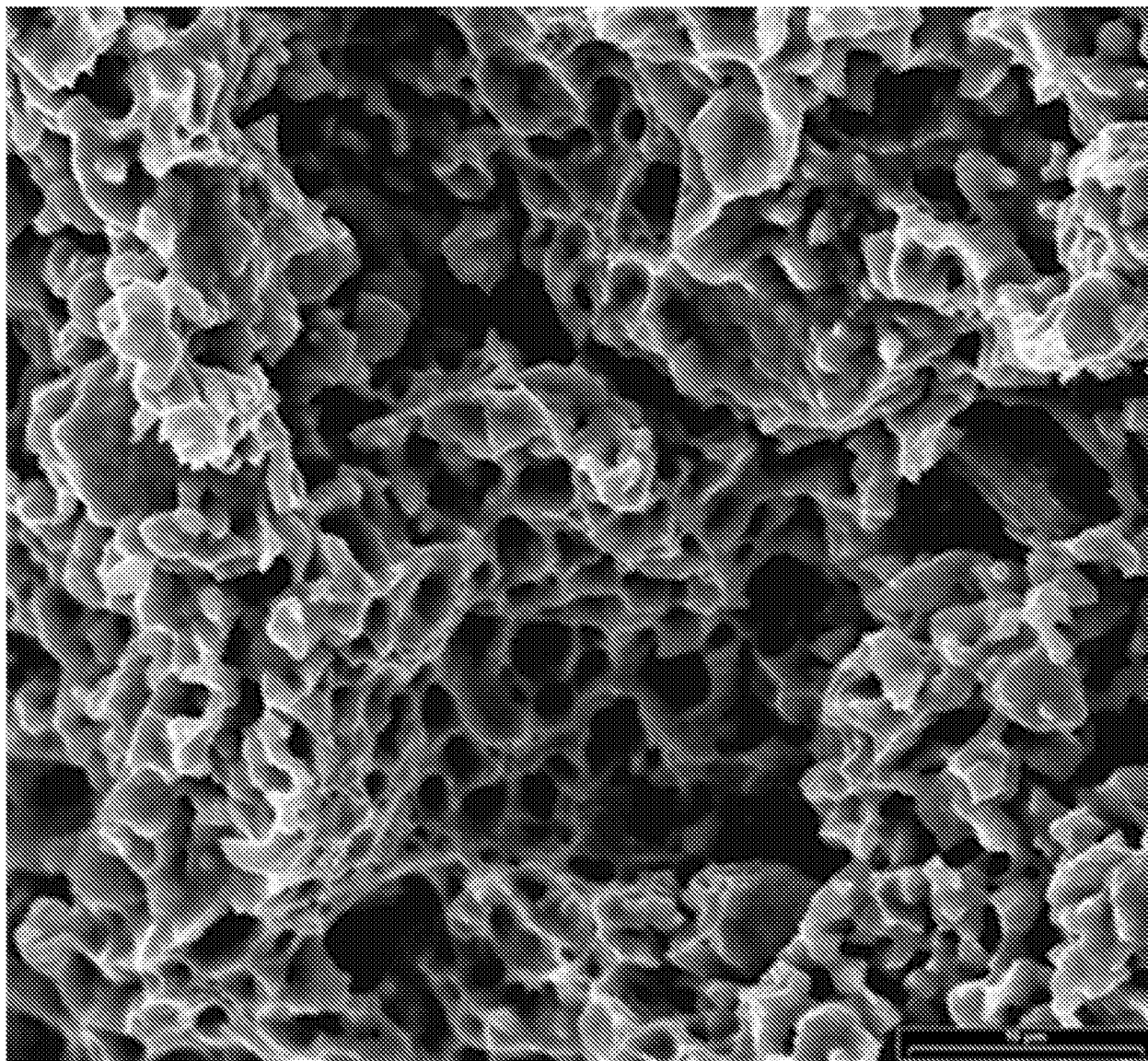


FIG. 5

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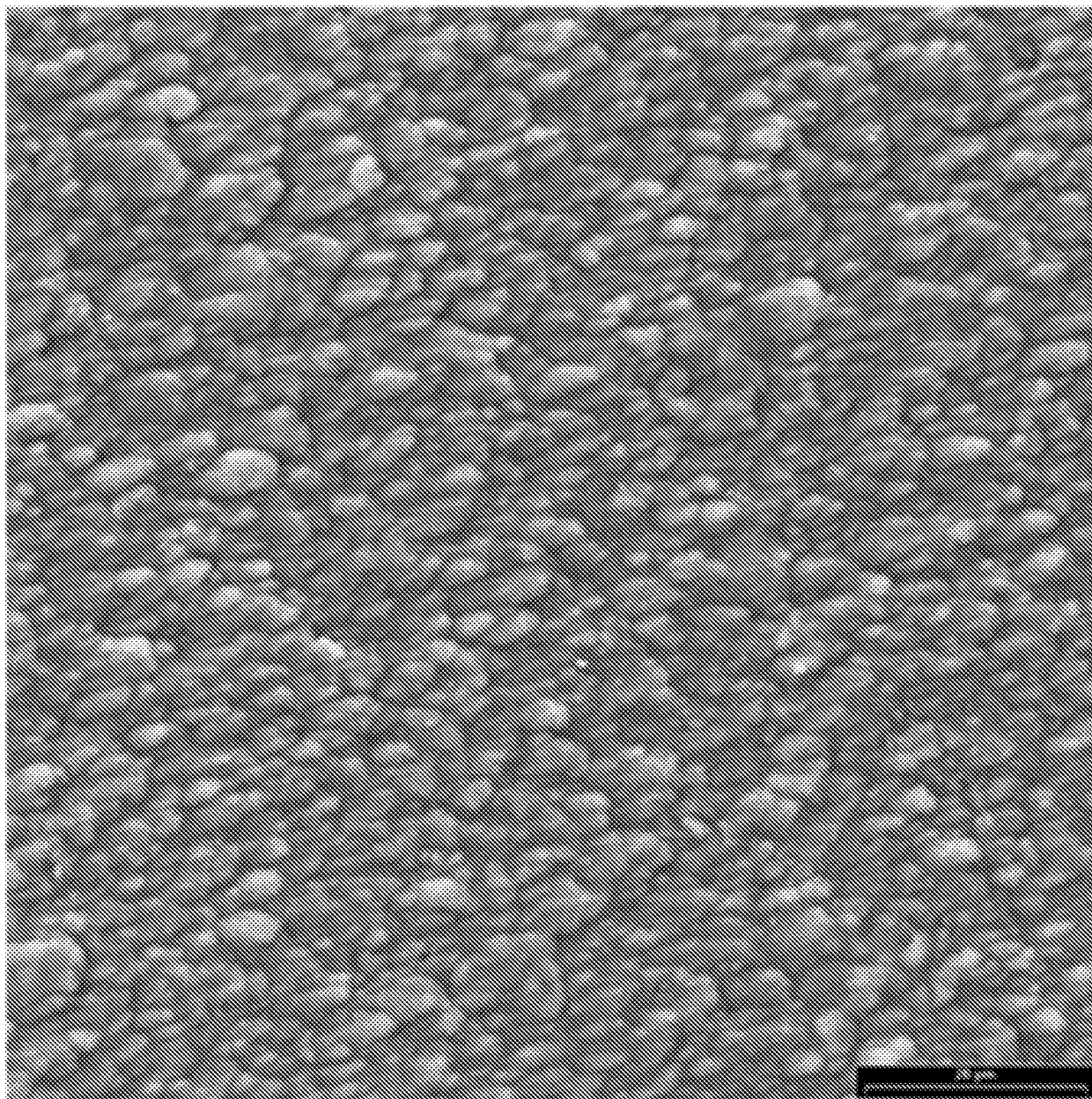


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/015671**A. CLASSIFICATION OF SUBJECT MATTER****H01M 4/86(2006.01)i, H01M 8/12(2006.01)i, H01M 8/02(2006.01)i**

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

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
H01M 4/86; H01M 8/12; C04B 35/64; H01M 8/00; H01M 2/00; H01M 4/92; H01M 8/02Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: solid oxide fuel cell (SOFC), porous metal anode, electrolytic layer, ceramic, cathode, nanopowder**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6869722 B2 (KEARL, D. A.) 22 March 2005 See abstract; columns 2-6 and 9; claims 1-13; and Figure 1.	1-26
X	US 2007-0072035 A1 (KOREVAAR, B. A. et al.) 29 March 2007 See abstract; paragraphs [0003], [0007] and [0034]-[0094]; claims 1 and 12-14.	1-16, 23-26
A	US 2012-0231366 A1 (WACHSMAN, E. D. et al.) 13 September 2012 See abstract; paragraphs [0011]-[0024]; and claims 1-5 and 8.	1-26
A	US 2012-0003565 A1 (SON, J.-W. et al.) 05 January 2012 See abstract; paragraphs [0049]-[0058]; and claims 1-5.	1-26
A	US 2013-0093128 A1 (KIM, C.-S. et al.) 18 April 2013 See abstract; paragraphs [0018]-[0038]; and claims 1-4.	1-26



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

06 July 2016 (06.07.2016)

Date of mailing of the international search report

06 July 2016 (06.07.2016)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

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Telephone No. +82-42-481-5405



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/015671

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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