



(51) International Patent Classification:
B82B 3/00 (2006.01) **B82B 1/00** (2006.01)

(21) International Application Number:
PCT/US2008/013333

(22) International Filing Date:
4 December 2008 (04.12.2008)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant (for all designated States except US): **UTC POWER CORPORATION** [US/US]; 195 Governor's Highway, South Windsor, CT 06074 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **OPALKA, Susanne, M.** [US/US]; c/o UTC Power Corporation, 195 Governor's Highway, South Windsor, CT 06074 (US). **VANDERSPURT, Thomas, Henry** [US/US]; c/o UTC Power Corporation, 195 Governor's Highway, South Windsor, CT 06074 (US).

(74) Agents: **FAIRBAIRN, David, R.** et al.; Kinney & Lange, P.A., The Kinney & Lange Building, 312 South Third Street, Minneapolis, MN 55415-1002 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— of inventorship (Rule 4.17(iv))

Published:

— with international search report (Art. 21(3))

(54) Title: METHOD OF PRODUCING A STABILIZED PLATINUM CATALYST WITH STRONG OXIDE FORMERS

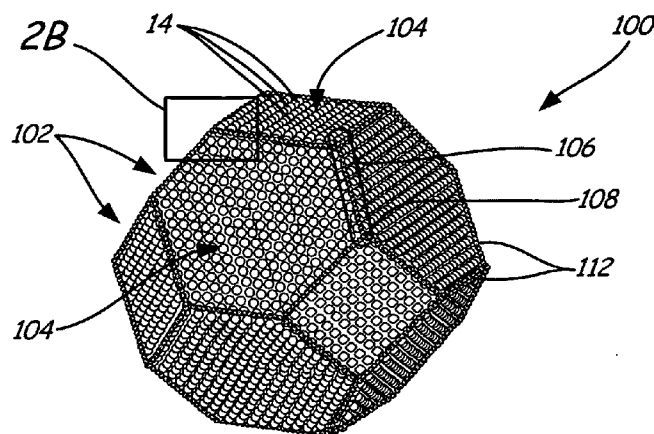


FIG. 2A

(57) Abstract: A nanoparticle has a core portion surrounded by a plurality of outer surfaces formed by terraces, edge regions and corner regions. The nanoparticle includes a plurality of platinum atoms and a plurality of atoms from a stabilizing metal. The platinum atoms form a plurality of terraces on the nanoparticle. The plurality of atoms from a stabilizing metal are located at edge regions and corner regions. The stabilizing metal includes at least one of zirconium, niobium, molybdenum, hafnium, tantalum and tungsten.

METHOD OF PRODUCING A STABILIZED PLATINUM CATALYST WITH STRONG OXIDE FORMERS

5

BACKGROUND

The present disclosure relates to platinum nanoparticles. More particularly, the present disclosure relates to stabilized platinum nanoparticles used as a catalyst in a fuel cell.

10

Platinum or platinum alloy nanoparticles are well known for use as an electrocatalyst, particularly in fuel cells used to produce electrical energy. For example, in a hydrogen fuel cell, a platinum catalyst is used to oxidize hydrogen gas into protons and electrons at the anode of the fuel cell. At the cathode of the fuel cell, the platinum catalyst triggers the oxygen reduction reaction (ORR), leading to formation of water. The ORR reaction takes place at high potential, which makes the platinum nanoparticles unstable on the cathode, resulting in a loss in electrochemical surface area of the nanoparticles. Due to potential cycling during fuel cell operation, the platinum nanoparticles may dissolve. The atoms at the corners and the edges of the nanoparticles have a higher surface energy and, as such, are more reactive than surface atoms on the terraces of the nanoparticles. The nanoparticles commonly include surface features or defects that form on the surface during synthesis of the nanoparticles. The atoms that form these surface defects, including steps and kinks, are also more reactive sites on the nanoparticle, compared to the surface atoms on the terraces. The more reactive atoms are more prone to forming oxides and dissolution, as compared to atoms having lower surface energy.

15

20

25

Although platinum is a preferred material for use as a catalyst in a fuel cell, platinum is expensive. Moreover, the instability of the platinum nanoparticles in the cathode environment results in a loss of surface area of the nanoparticles, and consequently a loss in fuel cell performance. This requires a larger amount of platinum catalyst to be used in the fuel cell, which increases cost. There is a need for a platinum nanoparticle that is more stable during long term operation as a cathode catalyst in a fuel cell.

30

SUMMARY

A nanoparticle has a core portion surrounded by a plurality of outer surfaces formed by terraces, edge regions and corner regions. The nanoparticle includes a plurality of platinum atoms and a plurality of atoms from a stabilizing metal. The platinum atoms form a plurality of terraces on the nanoparticle. The plurality of atoms from a stabilizing metal

35

are located at edge regions and corner regions. The stabilizing metal includes at least one of zirconium, niobium, molybdenum, hafnium, tantalum and tungsten, and mixtures thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

5 FIG. 1 is a schematic of a representative, existing platinum nanoparticle used, for example, as a catalyst, and having a plurality of terraces, corners and edges.

FIG. 2A is a schematic of a stabilized platinum nanoparticle having oxidized atoms from a stabilizing metal selectively located on edge and corner regions of the nanoparticle.

10 FIG. 2B is an enlarged view of a portion of the stabilized platinum nanoparticle of FIG. 2A.

FIG. 3 is a block diagram illustrating a method of producing a stable platinum nanoparticle similar to the nanoparticle of FIG. 2.

FIG. 4 is a plot of the reaction enthalpy for oxidative migration to different positions on a nanoparticle after deposition at an edge location.

15 FIG. 5 is a plot similar to FIG. 4 after deposition at a terrace location.

FIGS. 6A-6D are schematics illustrating the method of FIG. 3 for selectively locating oxidized stabilizing metal compounds at the edge and corner regions of the nanoparticle.

20 FIG. 7A is a schematic of an enlarged portion of a Pt (111) terrace of the nanoparticle of FIG. 6A having surface defects and randomly deposited stabilizing metal atoms.

FIG. 7B is a schematic of the Pt (111) terrace from FIG. 7A after oxidation and migration of the stabilizing metal atoms to the surface defects.

25 FIG. 8A is a schematic of a cubic-shaped nanoparticle that has undergone the process of FIG. 3 to form a stabilized nanoparticle.

FIG. 8B is an enlarged view of a portion of the stabilized platinum nanoparticle of FIG. 8A.

FIG. 9A is a schematic of a tetrahedron-shaped nanoparticle that has undergone the process of FIG. 3 to form a stabilized nanoparticle.

30 FIG. 9B is an enlarged view of a portion of the stabilized platinum nanoparticle of FIG. 9A.

FIG. 10 is a block diagram illustrating a method of producing a stable platinum nanoparticle having oxidized atoms from a stabilizing metal selectively located on edge and corner regions of the nanoparticle.

FIG. 11 is a schematic of a stabilized platinum nanoparticle produced by the process of FIG. 10.

FIGS 12A is a schematic of an enlarged portion of one a Pt (111) terraces of the nanoparticle of FIG. 11 to illustrate surface defects, including step atoms and kink atoms,
5 that may exist on the nanoparticle.

FIG. 12B is a schematic of the Pt (111) terrace from FIG. 12A after the platinum atoms at the surface defects have been selectively etched

FIG. 12C is a schematic of the Pt (111) terrace from FIG. 12B after stabilizing metal atoms have been selectively located and oxidized at the surface defects.

10 FIG. 13 is a schematic of a stabilized cubic-shaped nanoparticle, also suitable for use as a catalyst that has undergone the process of FIG. 11.

FIG. 14 is a schematic of a stabilized tetrahedron-shaped nanoparticle that has undergone the process of FIG. 11.

FIG. 15 is a schematic of a fuel cell that uses the platinum nanoparticles described
15 herein as a stabilized cathode catalyst.

It is noted that the drawings are not to scale.

DETAILED DESCRIPTION

A stabilized platinum nanoparticle is described herein which includes a stabilizing metal selected from the fifth and sixth rows of groups four, five and six of the periodic table
20 (zirconium (Zr), niobium (Nb), molybdenum (Mo), hafnium (Hf), tantalum (Ta) and tungsten (W)) located on select areas of an outer surface of the nanoparticle. For the purposes of this disclosure the term stabilizing metal includes the concept of a mixture of stabilizing metals. A method of producing stabilized nanoparticles is also described below and includes depositing stabilizing metal atoms on the nanoparticle, and oxidizing and
25 mildly annealing the nanoparticles so that oxidized stabilizing metal complexes are located at the edge and corner regions of the nanoparticles. Oxidized stabilizing metal complexes may also be located at surface defects on the nanoparticle, such as steps and kinks. Platinum nanoparticles are commonly used as a catalyst and the nanoparticle structure described herein results in a more stable catalyst. In one example, the platinum
30 nanoparticles may be used as a cathode catalyst for an oxygen reduction reaction (ORR) in a fuel cell. For the purposes of this disclosure the term platinum many include platinum rich alloys or platinum mixed metal clusters that are stable on the nano-scale.

Platinum nanoparticles may be produced using known synthesis methods, such as chemical reduction. The platinum nanoparticles may be prepared as colloidal particles, and

the size and shape of the nanoparticles may be controlled based on the conditions during synthesis. In one example in which the platinum nanoparticles are used as a catalyst, a suitable range for the diameter of the nanoparticles described herein is between approximately 0.5 and 100 nanometers (nm). In some examples, the diameter ranges
5 between approximately 1 and 20 nm; in other examples, the diameter ranges between approximately 1 and 10 nm.

FIG. 1 is a schematic of representative, existing nanoparticle 10, which has a cuboctahedron shape. Facetted cubic metal nanocrystals typically have a structure that falls within the range between cuboctahedra and truncated octahedra in shape. Nanoparticle 10
10 includes a core (or inside portion) and outer surfaces 12. In one example, surfaces 12 are formed from a plurality of platinum atoms 14 bonded together to create a plurality of flats or terraces 16, edges 18, and corners 19. Each edge 18 represents an intersection of two adjoining terraces 16, and each corner 19 is an intersection of at least three edges 18. As shown in FIG. 1, corners 19 represent an intersection of three edges 18. Platinum atoms 14
15 that form terraces are surface atoms. For purposes of this disclosure, in a Pt (111) facet or surface, a surface atom is defined as an atom having nine nearest neighbor atoms, since platinum has a face-centered cubic unit cell. Surface atoms have a lower surface energy than corner and edge atoms.

As shown in FIG. 1, nanoparticle 10 has a regular cuboctahedron shape, and terraces
20 16 are essentially flat and free of defects. It is recognized that nanoparticle 10 may commonly have a more irregular shape and terraces 16 may include surface features or defects, such as steps and kinks. These surface defects are described further below in reference to FIG. 7A.

Although not visible in FIG. 1, the core or inside portion of nanoparticle 10 can be
25 formed of platinum or a platinum alloy. Other metals used to form the platinum alloy core may include transition metals from periods 4, 5, and 6 of the periodic table. Alternatively, essentially all of the core of nanoparticle 10 can be formed by at least one metal other than platinum. In FIG. 1, outer surfaces 12 are formed essentially of platinum atoms 14. Depending on a composition of the core or inside portion, the platinum atoms that form
30 outer surfaces 12 may be formed from only one layer of platinum atoms. Alternatively, outer surfaces 12 may be formed from two or more layers of platinum atoms. In another example, all of nanoparticle 10, including outer surfaces 12, may be formed of a platinum alloy.

FIG. 2A is a schematic of strong oxide former stabilized nanoparticle 100, which has a cuboctahedron shape, and FIG. 2B is an enlarged view of a portion of stabilized nanoparticle 100. The stabilized nanoparticles described herein may include nanoparticles of any known shape; other example shapes are shown and discussed below. Similar to nanoparticle 10 of FIG. 1, nanoparticle 100 has a core portion and outer surfaces 102, which include terraces 104, edges 106 and corners 108. Similar to nanoparticle 10, core portion of nanoparticle 100 may be formed of platinum, a platinum alloy or at least one non-platinum metal, and terraces 104 are formed of platinum or platinum alloy atoms 14. In contrast to nanoparticle 10, oxidized stabilizing metal complexes 112 are located at edges 106 and corners 108. As shown in FIG. 2B, oxidized stabilizing metal complexes 112 are located on platinum atoms 14 at edges 106 and corners 108. Oxidized stabilizing metal complexes 112 have not replaced platinum atoms 14 at edges 106 and corners 108. Oxidized stabilizing metal complex 112 includes a stabilizing metal atom that is partially oxidized. The stabilizing metal atoms are transition metal atoms selected from the fifth and six rows of groups four through six of the periodic table (zirconium (Zr), niobium (Nb), molybdenum (Mo), hafnium (Hf), tantalum (Ta) and tungsten (W)) and combinations thereof. These transition metals are strong oxide formers. These transition metals do not readily form stable hydrated complexes in their lower oxidation states and are insoluble in acid in their highest oxidation state oxides. In contrast, oxidized transition metals from the fourth row of groups four through six of the periodic table (titanium (Ti), vanadium (V) and chromium (Cr)) have accessible lower oxidation states that are soluble under acidic conditions. The oxidized stabilizing metal complexes 112 may not be drawn to scale and the oxygen atoms are not shown explicitly on complexes 112.

As shown in FIG. 2A, nanoparticle 100, similar to nanoparticle 10 of FIG. 1, has a cuboctahedral shape and is essentially free of defects. As such, terraces 104 are formed essentially of all surface atoms. It is more common that nanoparticle 100 would have surface defects and some irregularity in its shape. For example, as described below the terraces may have steps that make each terrace an irregular surface.

FIG. 3 is a flow diagram illustrating method 200 for producing stabilized platinum nanoparticle 100 by depositing and migrating atoms of a stabilizing metal that is a strong oxide former to the edge and corner regions of the platinum nanoparticle. The stabilizing metal is a transition metal selected from the fifth and six rows of groups four through six of the periodic table (zirconium (Zr), niobium (Nb), molybdenum (Mo), hafnium (Hf), tantalum (Ta) and tungsten (W)) and combinations thereof. Method 200 begins with

obtaining platinum nanoparticles (step 202) similar to nanoparticle 10 of FIG. 1. The nanoparticles may be comprised essentially of platinum and platinum alloys, and may be of any known shape, as discussed further below. The platinum loading and the dispersion of the platinum particle size should be known. Step 202 of method 200 can include synthesis
5 of the platinum nanoparticles using any known method. Alternatively, the obtainment of the nanoparticles in step 202 can involve purchasing the platinum nanoparticles. The platinum nanoparticles can be supported in a substrate such as, but not limited to, carbon black, a metal oxide, a metal carbide, mixed metal carbide, boron doped diamond and combinations thereof. Alternatively, the platinum nanoparticles can be unsupported.

10 A next step in method 200 is to wash or flush the platinum nanoparticles with a non-aqueous, low surface tension solvent under an inert atmosphere (step 204). If the platinum nanoparticles are supported on a substrate, the substrate is submerged in the solvent during the wash. If the platinum nanoparticles are unsupported, they are dispersed in the solvent during the wash.

15 After washing the nanoparticles with the non-aqueous, low surface tension solvent, the suspension is flushed with hydrogen and a stabilizing metal complex solution is added (step 206). The stabilizing metal complex solution includes a solvent and low or zero valent compounds of a transition metal from the fifth and sixth rows of groups four through six of the periodic table. Example solvents include tetrahydrofuran (THF) and acetonitrile.
20 Suitable low or zero valent compounds include, but are not limited to: the cyclopentadiene $[M(\eta^5-C_5H_5)(CO)_2]$ where M is Zr or Hf, the cyclopentadiene $[M(\eta^5-C_5H_5)(CO)_4]$ where M is Nb or Ta, molybdenum carbonyl $[Mo(CO)_6]$ and tungsten carbonyl $[W(CO)_6]$. The stabilizing metal complex solution should contain a sufficient amount of low or zero valent compounds to completely coat or decorate the edge and corner regions of the nanoparticles
25 with stabilizing metal atoms as discussed below.

After adding the solution of low or zero valent compounds, the solution is mixed well. The pressure over the solution can be reduced or pulsed to insure that the nanoparticles fully imbibe the solution.

30 Next, stabilizing metal atoms are deposited on the nanoparticles (step 208). This can be accomplished by heating or refluxing the solution of low or zero valent compounds to just below the boiling point temperature. This heating may occur with stirring and under flowing hydrogen. In one example, 1 atm of hydrogen gas is introduced in the atmosphere. In another example where the stabilizing metal complex solution includes THF as a solvent, the temperature of the solution is kept below 66 °C, the boiling point of THF.

During the reflux of step 208, stabilizing metal atoms randomly deposit on the nanoparticle surfaces, (i.e. terraces, edges and corners). It is believed that the stabilizing metal atoms are deposited on the nanoparticles by mechanisms that are effectively reductive elimination mechanisms. It is believed that when the solution of low or zero valent compounds is refluxed in the presence of hydrogen, hydrogen attaches to the platinum atoms. Simultaneously or about simultaneously, the low or zero valent compounds adsorb on the nanoparticles. The adsorbed low or zero valent compounds contain at least one transition metal from the fifth and sixth rows of groups four through six of the periodic table. Because the stabilizing metal complex solution is in thorough contact with the nanoparticles, the molecular diffusion distance is small and the compounds adsorb on the nanoparticles on the order of minutes. Under the influence of mild heating and hydrogen, the adsorbed compounds decompose and deposit stabilizing metal atoms on the surfaces of the nanoparticles.

As described above, the deposition mechanism is believed to be effectively a reductive elimination. Reductive elimination involves the elimination or removal of a molecule from a transition metal complex so that the oxidation state of the transition metal complex is reduced. The mechanism in step 208 of method 200 is referred to as "effectively" a reductive elimination because while zirconium, hafnium, niobium and tantalum can be reduced, molybdenum and tungsten have an oxidation state of zero and thus, the oxidation state of these transition metals cannot be reduced. For example, when the compound is a cyclopentadiene of zirconium, hafnium, niobium or tantalum, the cyclopentadiene has an oxidation state of negative one (-1) and the transition metal (zirconium, hafnium, niobium or tantalum) has an oxidation state of plus one (+1). During the reflux, hydrogen removes a ligand from the compound and reduces the transition metal to an oxidation state of zero.

In contrast to zirconium, hafnium, niobium and tantalum compounds, the transition metals in molybdenum and tungsten carbonyls are already in the zero oxidation state. Nevertheless, molybdenum and tungsten transition metal atoms can be deposited. It is believed that the deposition occurs when hydrogen removes a ligand from the molybdenum or tungsten carbonyl. The removal of the ligand does not by definition reduce the transition metal because molybdenum and tungsten already are in the zero oxidation state, but the transition metal atoms are deposited.

As discussed above, refluxing the solution is only one example of a suitable stabilizing metal deposition method. Any deposition method that can deposit stabilizing

metal atoms on the outer surfaces of platinum nanoparticles can be used. Other example deposition methods include, but are not limited to, physical vapor deposition and chemical vapor deposition.

Following the deposition, the platinum nanoparticles are removed from the solution by suitable means, and dried under warm, flowing hydrogen (step 210). In one example, where the nanoparticles are unsupported and dispersed in the suspension, the solution is filtered to remove the nanoparticles from the suspension. In another example, where the nanoparticles are supported on a substrate, the substrate is removed from the solution.

The recovered platinum nanoparticles are mildly heated or annealed in a hydrogen containing atmosphere to remove any surface adsorbates, such as solvents (step 212). In one example where the low or zero valent compounds were mixed with THF, the nanoparticles can be heated to evaporate any THF that may have adsorbed during the reflux process. Mildly heating the recovered platinum nanoparticles also reduces any adsorbed low or zero valent compounds that were not previously reduced.

The platinum nanoparticles must be mildly heated in step 212 so that the deposited stabilizing metal atoms remain on the surface of the nanoparticle. If the platinum nanoparticles are annealed at too high of a temperature, the stabilizing metal atoms may migrate into the bulk or core region of the nanoparticle. In one example, the nanoparticles can be heated between about 100 °C and about 200 °C. In another example, the nanoparticles are heated to less than or equal to about two times the boiling point of the solvent to be removed. Migration into the bulk region of the nanoparticle is also caused by the length of annealing. In one example, the nanoparticles can be heated for about 1 hour or more. In another example, the nanoparticles can be heated for about 1 hour to about 24 hours. The length of annealing has an inverse relationship to the annealing temperature. The annealing process should be shorter at higher temperatures to prevent migration into the bulk. In one specific example, the nanoparticles are annealed for 24 hours at 100 °C. In another specific example, the nanoparticles are annealed for 1 hour at 200 °C. Lower temperatures are suggested for smaller platinum particle sizes.

Next, the stabilizing metal atoms on the nanoparticle are passivated (step 214). Passivation can include cooling the nanoparticles, such as to ambient temperature, completely replacing the hydrogen atmosphere with an inert gas, and then slowly introducing oxygen into the inert atmosphere so that the atmosphere contains about 10% oxygen or less. In one example, the inert gas contains about 3% oxygen or less. In another example, the inert gas contains about 1% oxygen or less. In a further example, the inert gas

contains between about 0.1% and about 1% oxygen. It is advisable to limit the temperature rise of the nanoparticles to under about 10 °C on exposure to oxygen containing gas.

The inert atmosphere having a low partial pressure of oxygen oxidizes the stabilizing metal atoms, and causes one or two oxygen atoms to attach to each deposited
5 stabilizing metal atom. The stabilizing metal atoms are partially oxidized to form oxidized stabilizing metal complexes; the stabilizing metals are not completely oxidized. The partial pressure of oxygen is controlled in order to control the rate of oxidation. Rapid oxidation of the nanoparticles will generate a large amount of heat, which can cause the nanoparticles to glow red and can decrease or destroy the catalytic properties of the nanoparticles.
10 Therefore, the partial pressure of oxygen is controlled to prevent the destruction of the nanoparticles.

After being passivated, the nanoparticles are mildly annealed in an inert atmosphere (step 216). In one example, the atmosphere is at least about 99.999% inert. During step 216, the nanoparticles are gradually warmed to between about 100 °C and about 150 °C.
15 The annealing process causes the partially oxidized stabilizing metal species to diffuse or migrate along the surface of the nanoparticle until they reach a preferred location, such as an edge or corner. All metal atoms (including platinum) diffuse, and diffusion is accelerated by the thermal effects of the annealing process. In step 216, the nanoparticles are mildly annealed to prevent the oxidized transition metal atoms from diffusing into the
20 bulk or core region of the nanoparticle. The oxygen atoms also assist in maintaining the stabilizing metal atoms on the surface of the nanoparticle during migration.

The inert annealing environment of step 216 is held for an effective period of time. In one example, the atmosphere is held until oxidized stabilizing metal complexes completely cover or decorate the edge and corner regions of the nanoparticles. In another
25 example, the atmosphere is held for between about 24 and 96 hours.

As discussed above, overall the oxidized stabilizing metal species will migrate on the surface of the nanoparticle from a first location to a stabilizing location that is more favorable than the first location. The degree of favorability of a location or site is determined by the reaction enthalpy for oxidation and migration. FIGS. 4 and 5 illustrate
30 the reaction enthalpies (in kJ/mol) for oxidation and migration of a stabilizing metal atom initially deposited on an edge region and a terrace region of a platinum nanoparticle, respectively. Negative values of increasing magnitude indicate increasing favorability. The reaction enthalpies provided in FIGS. 4 and 5 were achieved through Vienna Ab-initio Simulation Package (VASP) atomistic modeling.

As seen in FIGS. 4 and 5, the stabilizing metal atoms that are deposited either on an edge or on a terrace of the platinum nanoparticle will favor edge locations compared to terrace and subsurface locations. During surface migration, a stabilizing metal atom will move from a first location to second location if the second location has a more favorable reaction enthalpy for oxidation and migration than the first location. Therefore, according to FIGS. 4 and 5, atoms of the listed stabilizing metals will continue to migrate during step 216 until each atom reaches an edge. Each stabilizing metal atom deposited on the surface of the nanoparticle will migrate to an edge position or a similarly favorable location regardless of where they were originally deposited. Similarly, a stabilizing metal atom deposited at the edge will remain at the edge during step 216 because it is the most favorable location.

FIGS. 4 and 5 illustrate the reaction enthalpies for oxidation and migration to edge, terrace and subsurface sites. It should be noted that in this modeling, "edge" includes edges, corners and surface defect locations due to the similar reactivity and stability of atoms at these locations. The stability of an atom depends, in part, on the number of surrounding atoms. Atoms at edge, corner and surface defect locations have less surrounding atoms than atoms at terraces or flats, thus making the edge, corner and surface defect locations more reactive. During migration and oxidation, the transition metal atoms of zirconium (Zr), niobium (Nb), molybdenum (Mo), hafnium (Hf), tantalum (Ta) and tungsten (W) will favor and will migrate to the platinum edge, corner and surface defect atoms of the nanoparticle regardless of where the stabilizing metal atoms are originally deposited.

Following step 216, the oxidized stabilizing metal complexes should completely cover or decorate all of the edge and corner regions of the nanoparticles. To accomplish this, the number of oxidized stabilizing metal complexes necessary to cover the edge and corner regions must be estimated to determine the concentration of the metal compound solution refluxed with the nanoparticles in step 208. The necessary amount of oxidized stabilizing metal complexes depends upon the atomic fraction of edge and corner atoms on the nanoparticles and the average radius of the oxidized stabilizing metal complexes. The atomic fraction of edge and corner atoms can be estimated based on: the mass of the catalyst (support plus nanoparticles) to be treated, (M); the weight percentage of platinum alloy present in the catalyst, (W); the effective density of the platinum alloy, (P); and the average platinum alloy nanoparticle diameter in nm, (D). The nanoparticle diameter can be estimated based on the platinum loading and the dispersion of the nanoparticles. In another

example, the nanoparticle diameter (or crystallite size distribution) is determined by other suitable means such as by a scanning electron microscope (SEM) or a transmission electron microscope (TEM).

In order to estimate the number of edge and corner atoms on the nanoparticle, the mass of platinum on the nanoparticles (m_m) and the volume of platinum on the nanoparticles (v_m) are first calculated as follows.

$$(1) m_m = M(W/100)$$

$$(2) v_m (\text{in cm}^3) = m_m/P$$

Assuming that the platinum atoms are hemispheres, the volume of a platinum atom (v_p) and the number of platinum atoms on the nanoparticles (n_p) are calculated as follows:

$$(3) v_p = 0.074D^3$$

$$(4) n_p = v_m/v_p$$

Assuming the principal metal in the nanoparticles is platinum with a nominal atomic diameter of 0.276 nm, there are approximately four platinum atoms per nanometer of edge length. Assuming that the platinum atoms nanoparticles are supported on a substrate so that each nanoparticle is a faceted hemispherical dome similar to half of a cuboctahedron with 16 edges, there would be approximately 64 platinum edge and corner atoms per nanometer of nanoparticle edge length (4 atoms per edge length times 16 edges, assuming that corner atoms will be located along and are included in the edge length).

Next, a radius ratio factor (R) is calculated. The radius ratio factor is necessary because the radius of platinum (r_p) is slightly larger than the radius of the oxidized stabilizing metal complexes (r_m).

$$(5) R = r_p/r_m$$

A radius table, as shown in Table 1, can be used to estimate r_p and r_m . (Radius table from: Francis S. Galasso, Structure and Properties of Inorganic Solids 8-11 (Pergamon Press 1970)). Because the stabilizing metal is only partially oxidized, the exact radius of the complex will not be available in a table. However, the radius can be estimated by the +4 oxidation state. For example, where the oxidized complex contains Nb, the radius ratio factor is $0.138/0.074 = 1.9$. This estimation will slightly overstate the amount of oxidized stabilizing metal complexes (and stabilizing metal atoms) necessary to completely coat the edge and corner regions of the nanoparticles. However, this over estimation accounts for imperfect deposition and other factors as is discussed below.

TABLE 1

Metal	Partially oxidized r_m in nm	Oxidation state
Zr	0.080	+4
Nb	0.074	+4
Mo	0.070	+4
Hf	0.078	+4
Ta	0.074	+4
W	0.070	+4

Finally, the target amount of moles of stabilizing metal necessary to cover the edge and corner regions of the nanoparticles and the required concentration of the solution are calculated by the following:

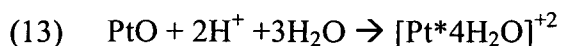
(6) Moles of stabilizing metal = $72R_n D/N_a$, wherein N_a is 6.022×10^{23}

(7) Concentration of solution = moles of stabilizing metal/volume of solution

As discussed above, this estimated target amount will overstate the amount of oxidized stabilizing metal complexes and moles of stabilizing metal necessary to completely cover the edge and corner regions of the nanoparticles. The extra amount of stabilizing metal accounts for estimation errors, imperfections in deposition and the affinity of the low or zero valent compounds to the substrate support. Additionally, the extra amount accounts for locating oxidized stabilizing metal complexes at surface defect locations (i.e. steps and kinks) as will be discussed later. In one example, 20% more than the estimated target amount of moles of stabilizing metal is present in the solution. In another example, up to twice the estimated target amount of moles of stabilizing metal is added to the solution. Solubility limitations may arise for high concentrations of stabilizing metals and can typically be overcome by changing solvents.

Method 200 of FIG. 3 is a deposition and migration process. A platinum nanoparticle can have oxidized complexes from at least one transition metal from the fifth and sixth rows of groups four through six of the periodic table (titanium, vanadium, chromium, zirconium, niobium and molybdenum) located at the corner and edge regions to form a stabilized platinum nanoparticle using method 200. When platinum nanoparticles are used as catalysts, the platinum atoms at the corners and edges of the nanoparticle are susceptible to dissolution. These atoms are attributed to being the primary sites for promoting loss in electrochemical surface area (ECA) during potential cycling under acidic oxidizing conditions (the conditions present in a hydrogen fuel cell). VASP atomistic modeling predicts that the selective population of these vulnerable platinum nanoparticle

sites with oxidized atoms from at least one of the transition metals of zirconium, niobium, molybdenum, hafnium, tantalum and tungsten will stabilize the platinum nanoparticle against platinum loss under acidic oxidizing conditions. Table 2 gives the predicted platinum oxide (PtO) dissolution enthalpies from non-stabilized and transition metal stabilized platinum edges and terraces for the reaction:



The stabilizing metals dramatically increase the dissolution enthalpies for the PtO dissolution reactions of adjacent platinum atoms. This indicates significantly less favorable (more positive or endothermic) PtO dissolution compared to the non-stabilized case.

TABLE 2

TM	Remove PtO Adjacent to Transition Metal (TM) on	
	(111)x(111) Edge	(111) Terrace
	(kJ/mole)	(kJ/mole)
None	98.4	-
Zr	545.1	244.3
Hf	643.1	272.0
Nb	558.6	293.5
Ta	674.4	332.2
Mo	517.8	296.2
W	614.8	434.1

The selective population of strong oxide former transition metals (Zr, Hf, Nb, Ta, Mo and W) prevents dissolution of the platinum atoms and loss of ECA. Their presence stabilizes adjoining nanocrystallite surfaces and protects adjacent platinum terrace atoms from dissolution at high potentials by locally increasing the platinum alloy stability and decreasing the surface energy. Additionally, these oxidized transition metals are notably insoluble in acid and do not form low oxidation state (+2 or +3) aquo-ions.

As discussed above, VASP atomistic modeling predicts that when oxidized, the atoms of transition metals of the fifth and sixth rows of groups four through six of the periodic table will preferentially populate the platinum atoms at the edges, corners and surface defects of the nanoparticle in order to complete their coordination sphere. Thus, oxidation and annealing will promote selective stabilizing metal surface migration to the edge and corner regions to achieve the desired protective and stabilizing configuration. These results are surprising because transition metals of the fifth and sixth rows of groups

four through six of the periodic table are high melting refractory elements that are generally believed to be more stable bulk substituents and less stable at the surface of lower melting elements, such as platinum. These results are also surprising and non-obvious to one skilled in the art in that these metals though refractory are considered less noble than Pt.

5 Platinum nanoparticles can be processed using method 200 during any stage of electrode fabrication so long as unstabilized platinum atoms are accessible to the adsorbing stabilizing metal atoms. For example, platinum oxidation would make the platinum atoms inaccessible because the oxygen atoms bound to platinum would prevent stabilizing metal atoms from directly depositing on the platinum atoms. Oxidized platinum is soluble under
 10 strong oxidizing condition. Therefore, the oxidized platinum will dissolve when the nanoparticles are used as a catalyst, and the ECA would be reduced. In contrast, the platinum nanoparticles may be inaccessible because of a substrate. In this situation, the platinum atoms will remain attached to the substrate even under strong oxidizing conditions. The substrate stabilizes the platinum atoms and they are less susceptible to dissolution.
 15 Therefore, it may not be necessary to stabilize these platinum atoms with stabilizing metal atoms.

FIG. 6A-6D are schematics showing how nanoparticle 10 of FIG. 1 is believed to undergo method 200 to form nanoparticle 100 of FIG. 2. FIG. 6A shows nanoparticle 10, which is initially formed only of platinum atoms 14, exposed to low or zero valent
 20 compounds 300 of a stabilizing metal from the fifth and sixth rows of groups four through six of the periodic table (step 206). Suitable compounds include, but are not limited to: the cyclopentadiene $[M(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ where M is Zr or Hf, the cyclopentadiene $[M(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_4]$ where M is Nb or Ta, molybdenum carbonyl $[(\text{Mo}(\text{CO})_6)]$ and tungsten carbonyl $[(\text{W}(\text{CO})_6)]$.

25 As shown in FIG. 6B, compounds 300 adsorb on the nanoparticle. Under the influence of hydrogen and heat, compounds 300 are reduced and stabilizing metal atoms 302 are deposited on the nanoparticle. As illustrated, stabilizing metal atoms 302 randomly deposit on the surface of the nanoparticle and can be deposited on terraces 16, edges 18 and corners 19.

30 FIG. 6C is an enlarged view of an edge portion of the nanoparticle. As illustrated in FIG. 6C, deposited stabilizing metal atoms 302 are oxidized by oxygen atoms 304 to form oxidized stabilizing metal complexes 112. Together atoms 302 and 304 migrate to the edge and corner regions of the nanoparticle. As FIG. 6C shows, two adjacent stabilizing metal atoms 302 will share an oxygen atom 304 so that oxygen atoms 304 are bridge-bonded to

stabilizing metal atoms 302. FIG. 6D is a schematic of nanoparticle 100 when oxidized stabilizing metal complexes 112 are located at and cover essentially all the corner and edge regions of nanoparticle 100; thus nanoparticle 10 is converted to nanoparticle 100. It is recognized that nanoparticle 100 may have a slightly irregular shape due to a difference in size between platinum atoms and partially oxidized stabilizing metal complexes.

In one example, the stabilizing metal located on the platinum atoms is niobium (Nb). Although platinum is a noble metal, in operation as catalyst in a fuel cell, platinum atoms on the platinum nanoparticle are unstable and may be oxidized. This causes the platinum atoms to dissolve from the nanoparticle, resulting in an unstable platinum catalyst. The oxidized cyclopentadiene of niobium is well suited for this application because the oxidized complex stabilizes the adjoining nanocrystallite surfaces and is insoluble in acid (i.e. during operation of the fuel cell). By locating this oxidized complex at the edges and corners of the nanoparticle, the edge and corner regions of the nanoparticle do not dissolve during operation of the fuel cell and the catalyst remains stable over time.

Moreover, if only the corners and edge regions of the nanoparticle are covered with niobium, the impact on the ORR activity of the platinum catalyst is negligible. As shown in FIG. 6D, oxidized stabilizing metal complexes 112 essentially completely cover the edge and corner regions of nanoparticle 100. In FIG. 6D, nanoparticle 100 is large enough such that the majority of the total surface area of nanoparticle 100 is still formed by platinum atoms 14. For smaller sized nanoparticles, which have less platinum atoms on each terrace, the oxidized stabilizing metal complexes that cover or decorate the edge and corner regions occupy a greater portion of the total surface area of the nanoparticle. As mentioned above, in one example, a suitable range of the diameter of the platinum nanoparticles is between approximately 1 and 20 nm; in another example, the diameter ranges between approximately 1 and 10 nm. For smaller-sized nanoparticles (i.e. less than 1.5 nm), the oxidized stabilizing metal complexes occupy more of the surface area of the nanoparticle. As such, the oxidized stabilizing metal complexes may occupy up to approximately seventy-five percent of the total surface area of the nanoparticle. On the other hand, nanoparticles up to or greater than 10 nanometers may also be used, and thus the oxidized stabilizing metal complexes may occupy as little as approximately five percent of the total surface area. Therefore, once the stabilizing metal atoms are oxidized on the surface, the oxidized stabilizing metal complexes may occupy between approximately five and approximately seventy-five percent of a total surface area of the nanoparticle.

The nanoparticles shown thus far have had regular cuboctahedron shapes and have been essentially free of defects. As such, the terraces of the nanoparticles have been shown as flat surfaces comprised essentially of all surface atoms. As stated above, in reality, the nanoparticles described herein commonly have surface defects that form as a result of the synthesis process used in forming the nanoparticles. FIG. 7A is a schematic of an enlarged portion of one of terraces 16 from nanoparticle 10 of FIG. 6A to illustrate these surface defects. Terrace 16 of FIG. 7A is a (111) surface. FIGS. 7A and 7B illustrate that if surface defects are present on a nanoparticle, atoms of a stabilizing metal from the fifth and sixth rows of groups four through six of the periodic table may likely migrate to the platinum atoms at the surface defects. (Note that the surface defects shown in FIG. 7A are not visible in FIG. 6A). As discussed above with respect to FIGS. 4 and 5, the reaction enthalpy to oxidize and anneal a stabilizing metal atoms to a surface defect is more favorable (i.e. has a greater negative reaction enthalpy) compared to reaction enthalpies for terrace and subsurface sites.

As shown in FIG. 7A, Pt (111) terrace 16 is formed of all platinum atoms 14 and includes stable portion 16a and ledge 66. Step 66 is a layer of platinum atoms 14 that forms over part of stable portion 16a, resulting in an elevated layer of atoms 14. Similar to atoms 14 on stable portion 16a, the majority of atoms 14 on ledge 66 are surface atoms. Because platinum has a face-centered cubic unit cell, a surface atom on a (111) surface has nine nearest neighbor atoms. The stability of each atom is a function, in part, of how many other atoms are surrounding that atom. Like the surface atoms in stable portion 16a, most atoms on ledge 66 have nine nearest neighbor atoms. However, platinum atoms 14 located in a last row of ledge 66 (labeled as 66a) are more reactive because these atoms have no more than seven nearest neighbor atoms. More specifically, last row 66a includes step atoms 67, kink atom 68 and step adatom 69. Step atoms 67 are defined as atoms having seven nearest neighbor atoms. Kink atom 68 has six nearest neighbor atoms, including a step atom 67. Finally, step adatom 69 has only five nearest neighbor atoms. It is recognized that the nearest neighbor atoms for surface atoms, step atoms, kink atoms and step adatoms will vary based on the crystallographic orientation of the facet surface, where the (111) surfaces shown in Figs. 7A and 7B have the closest possible packing with the greatest number of neighbors to surface atoms.

FIG. 7A shows randomly deposited stabilizing metal atoms 302 about to be oxidized by oxygen atoms 304. As described above, low or zero valence compounds adsorb on the nanoparticle, and are effectively reduced so that stabilizing metal atoms 302 deposit on the

outer surface of the nanoparticle. Oxygen atoms 304 attach to stabilizing metal atoms 302 to form oxidized stabilizing metal complexes 112. Mild annealing causes oxidized complexes 112 to migrate on the outer surface of the nanoparticle to the surface defect locations. This migration is caused by the difference in reaction enthalpies of the outer surface and the surface defect locations. Oxidized complex 112 will continually migrate to a location that is more favorable than the location it currently occupies. VASP atomistic modeling predicts that edge locations are more favorable locations for oxidized stabilizing metal complexes 112 compared to terrace and subsurface locations. Further, surface defect sites and edge sites have similar stabilities because the stability of an atom depends, in part, on the number of atoms surrounding it and these sites have fewer surrounding atoms than atoms on terraces or a subsurface. Therefore, due to the similar stability and reactivity of edge and surface defect atoms, it is believed that the oxidation and migration of a stabilizing metal atom to a surface defect location will have a reaction enthalpy similar to an edge location so that oxidized complex 112 will continue to migrate on the surface of the nanoparticle until it reaches an edge, corner or surface defect region. Overall, a movement of oxidized complex 112 from the terraces to edge, corner and surface defect regions will be seen during the annealing process.

FIG. 7B shows Pt (111) terrace 16 after oxidized stabilizing metal complexes 112 have migrated to platinum atoms 66a, which are located on the last row of ledge 66. As shown in FIG. 7B, oxidized stabilizing metal complexes 112 migrate to step adatom 69, kink atom 68 and step atoms 67. The solution used during deposition of the stabilizing metal atoms should contain at least enough stabilizing metal atoms so that oxidized stabilizing metal complexes can completely cover the edge, corner and surface defect regions of the nanoparticles. Additionally, it is recognized that multiple ledges and steps may be present on terrace 16, including multiple ledges adjacent to one another. The nanoparticles described herein may vary in terms of an amount of surface defects present on the nanoparticles.

As described above, the nanoparticles are annealed for a time sufficient such that the oxidized stabilizing metal complexes migrate from the terraces, which have a less favorable reaction enthalpy for oxidization and migration, to the edge, corner and surface defect regions. More specifically, the platinum surface atoms on the terraces are not covered by oxidized stabilizing metal complexes. By contrast, oxidized stabilizing metal complexes may likely be located at the platinum atoms that form the steps and kinks on the terraces, because these locations have more favorable reaction enthalpies than terrace locations.

Unless a nanoparticle has an unusually large number of surface defects, the majority of the terraces should remain unchanged. Depending on an amount of surface defects, the oxidized stabilizing metal complexes may occupy a greater percentage of the surface area of the nanoparticle than the ranges provided above, which were based on the edge and corner regions of the nanoparticle.

FIG. 8A is a schematic of stabilized cubic-shaped nanoparticle 400, which is similar to stabilized nanoparticle 100 of FIG. 2, but is cubic-shaped. Nanoparticle 400 has a core formed of platinum, a platinum alloy or at least one other stabilizing metal. Outer surfaces 402 of nanoparticle 400 are formed of platinum atoms 404 and include flats or terraces 406, edges 408 and corners 409. Nanoparticle 400, as shown in FIG. 8A, has a cubic shape, and terraces 406 are generally free of defects. However, it is recognized that nanoparticles commonly have surface defects or features that result in nanoparticle 400 having an irregular shape and terraces 406 having uneven surfaces. Stabilized nanoparticle 400 has already undergone method 200 of FIG. 3 so that terraces 406 are formed from platinum atoms 404 and oxidized stabilizing metal complexes 410 are located at edges 408 and corners 409.

In order to form nanoparticle 400, a cubic-shaped nanoparticle having all outer surfaces formed of platinum atoms is combined with a solution containing compounds of a stabilizing metal from the fifth and sixth rows of groups four through six of the periodic table (zirconium, niobium, molybdenum, hafnium, tantalum and tungsten). The compounds adsorb on the nanoparticle, and under the influence of heat and hydrogen, the compounds are effectively reduced so that stabilizing metal atoms are deposited on the nanoparticle. The compounds adsorb randomly on the nanoparticle and can adsorb on terraces 406, edges 408 and corners 409. Similarly, the stabilizing metal atoms are deposited randomly on the nanoparticle and can be deposited on terraces 406, edges 408 and corners 409. After deposition, the stabilizing metal atoms are partially oxidized to form oxidized stabilizing metal complexes 410, and the nanoparticle is mildly annealed so that oxidized stabilizing metal complexes 410 migrate to edges 408 and corners 409.

FIG. 8B is an enlarged view of a portion of stabilized cubic-shaped nanoparticle 400. Oxidized stabilizing metal complexes 410 are smaller in size than platinum atoms 404, although the difference in size may not be to scale in FIG. 8B. An overall size of nanoparticle 400 remains unchanged compared to a cubic-shaped platinum nanoparticle without oxidized stabilizing metal complexes 410, particularly since the oxidized complexes are small and they cover the platinum atoms only at the edges and corners. It is recognized

that nanoparticle 400 may have an irregular shape compared to a cubic-shaped nanoparticle without oxidized stabilizing metal complexes 410; however, nanoparticle 400 remains generally cubic-shaped. Although not shown in FIGS. 8A and 8B, it is recognized that nanoparticle 400 may include surface defects, such as steps and kinks, on terraces 406. As discussed above, the platinum atoms that form surface defects, such as steps and kinks, have a reactivity similar to that of the platinum atoms at edge 408 and corners 409. As such, the platinum atoms at the surface defects may also be replaced with oxidized stabilizing metal complexes 410.

FIG. 9A is a schematic of stabilized nanoparticle 500, similar to stabilized nanoparticles 100 and 400, but having a tetrahedron shape. Nanoparticle 500 is formed of a core portion and outer surfaces 502. Outer surfaces 502 are formed of platinum atoms 504 and include terraces 506, edges 508 and corners 509. It is recognized that nanoparticle 500, in reality, may have a more irregular tetrahedron-based shaped, and that surface defects (i.e. steps and kinks) may be present on terraces 506.

Nanoparticle 500 has already undergone method 200 of FIG. 3 to form a stabilized nanoparticle having oxidized stabilizing metal compounds 510 located at edges 508 and corners 509. As described above, when a nanoparticle having all outer surfaces formed of platinum atoms is combined with stabilizing metal compounds in solution, the stabilizing metal compounds adsorb on the nanoparticle. Under the influence of heat and hydrogen, the adsorbed stabilizing metal compounds are reduced and deposit stabilizing metal atoms. Then the stabilizing metal atoms are partially oxidized to form oxidized stabilizing metal complexes 510, and the nanoparticle is mildly annealed so that oxidized stabilizing metal complexes 510 migrate to edges 508 and corners 509 of the nanoparticle.

After oxidation and mild annealing, oxidized stabilizing metal complexes 510 essentially covered all platinum atoms 504 at edge and corner regions 508 and 509 to form stabilized nanoparticle 500. Nanoparticle 500 can have an irregular shape due to a difference in size between platinum atoms 504 and oxidized stabilizing metal complexes 510. Since nanoparticles can have surface defects on terraces 506, it is recognized that nanoparticle 500 can also include oxidized stabilizing metal complexes on terraces 506 such that oxidized stabilizing metal complexes 510 cover the platinum atoms forming the surface defects (i.e. steps, kinks).

FIG. 9B is an enlarged view of an edge of nanoparticle 500. FIG. 9B illustrates the size differential between platinum atoms 504 and oxidized stabilizing metal complexes 510 that cover platinum atoms 504 at edges 508 and corners 509. It should be noted that

although oxidized stabilizing metal complexes 510 are smaller than platinum atoms 504, the figures are not to scale. Further, the individual oxygen and stabilizing metal atoms of oxidized stabilizing metal complexes 510 are not shown. FIG. 9B also illustrates that oxidized stabilizing metal complexes 510 cover platinum atoms 504 at edges 508 and corners 509; platinum atoms 504 are not removed and replaced by oxidized stabilizing metal complexes 510.

FIG. 10 is a flow diagram illustrating an alternative method 600 for producing a strong oxide former stabilized nanoparticle. In method 600, platinum atoms at the edge and corner regions of the nanoparticle are selectively removed and replaced with atoms of a strong oxide former stabilizing metal, which is then oxidized. The stabilizing metal is selected from the fifth and six rows of groups four through six of the periodic table (zirconium (Zr), niobium (Nb), molybdenum (Mo), hafnium (Hf), tantalum (Ta) and tungsten (W)) and combinations thereof. These stabilizing metals are strong oxide formers, and they do not dissolve even under strong oxidizing conditions.

Method 600 begins with obtaining a platinum electrode (step 602). The electrode is a platinized electrode that is plated with platinum nanoparticles similar to nanoparticle 10 of FIG. 1. The nanoparticles may be comprised essentially of platinum and platinum alloys, and may be of any known shape, as discussed above. Step 602 of method 600 may include obtaining the nanoparticles and fabricating the electrode. The nanoparticles may be synthesized using any known method or may be purchased. One method to prepare a platinized electrode includes forming a catalyst ink containing platinum nanoparticles and applying the ink to a gas diffusion membrane layer, such as polytetrafluoroethylene (PTFE) sheets.

In step 604, the electrode is operated under platinum dissolution conditions, such as under a high potential, in a liquid electrolyte to selectively etch the platinum nanoparticles on the platinized electrode. The electrode should be selectively etched so that the platinum edge and corner atoms are removed from the nanoparticles. In one example, the applied potential is about 1.2 volts. Suitable liquid electrolytes include any strong acid that is favorable to dissolving platinum. In one example, the liquid electrolyte is a sulfuric acid solution. In another example, the liquid electrolyte is a sulfonic acid solution.

Platinum atoms will be etched or removed first at the corner and edge regions of the nanoparticle due to the increased susceptibility of these atoms to dissolution. The susceptibility of a platinum atom to dissolution increases as the number of nearest neighbors decreases. Over time, the electrolyte will also remove the platinum atoms on the terraces or

flats of the nanoparticle. However, the platinum atoms on the terraces are less susceptible to dissolution compared to atoms at the corners and edge regions. As described below, the nanoparticles are only left in the solution for a certain period of time in order to prevent the removal of the platinum atoms on the terraces of the nanoparticle.

5 In step 606, the etching process is stopped by removing the dissolution conditions. The etching process should be stopped after a time determined to be sufficient to remove the platinum atoms essentially only on the edge and corner regions of the nanoparticle, such that the terraces remain unchanged. In one example, the etching process is stopped after about four to five minutes. The length of etching depends upon many factors such as the
10 number of platinum edge atoms, the size of the nanoparticles and the applied potential. To stop the etching process, the electric current is stopped and the electrolyte is removed by flushing the electrode with an aqueous solvent, such as deoxygenated double distilled water. Any reactive gas in the atmosphere can be replaced with inert gas. After flushing the electrode with an aqueous solvent, the electrode is flushed with an oxygen-free, water-
15 miscible solvent, followed by THF. Example dissolved oxygen-free, water-miscible solvents include an alcohol such as acetone, ethanol and iso-propanol.

In step 608, a stabilizing metal is deposited on the nanoparticles. Step 608 includes forming a solution of stabilizing metal compounds, suspending the electrode in the solution and depositing stabilizing metal atoms. First, stabilizing metal compounds are mixed with a
20 low surface tension solvent such as, but not limited to, THF, to form a solution of stabilizing metal compounds. The stabilizing metal compounds are low or zero valent compounds of at least one stabilizing metal from the fifth and sixth rows of groups four through six of the periodic table. Example stabilizing metal compounds include, but are not limited to: the cyclopentadiene $[M(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ where M is Zr or Hf, the
25 cyclopentadiene $[M(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_4]$ where M is Nb or Ta, molybdenum carbonyl $[(\text{Mo}(\text{CO})_6)]$ and tungsten carbonyl $[(\text{W}(\text{CO})_6)]$. As will be described below, the stabilizing metal compounds decompose and deposit stabilizing metal atoms on the nanoparticles. The solution must contain a sufficient amount of low or zero valent compounds so that stabilizing metal atoms completely cover the locations vacated by the etched platinum
30 atoms.

Next, the electrode is suspended in the solution. The pressure over the solution can be reduced or pulsed to insure that the nanoparticles fully imbibe the solution. Then, the solution is heated or refluxed to deposit the stabilizing metal atoms on the nanoparticles. In one example where the solvent is THF, the temperature of the solution is kept below is 66

°C, which is the boiling point of THF, during the reflux. The reflux may occur with stirring and under flowing hydrogen. The stability of each platinum atom is a function, in part, of how many other atoms are surrounding that atom. Therefore, after the etching process, some of the most active sites on the nanoparticles will be the etched edge and corner regions with the fewest number of nearest neighbors and the stabilizing metal atoms will preferentially deposit here. Other suitable deposition methods include, but are not limited to, physical vapor deposition and chemical vapor deposition.

Following the deposition of the stabilizing metal atoms, the electrode is removed from the reflux solution, and dried under warm, flowing hydrogen (step 612). Then, the electrode is mildly heated or annealed in a hydrogen containing atmosphere to remove any surface adsorbates, such as solvents (step 614). The platinum nanoparticles must be mildly annealed so that the deposited stabilizing metal remains on the surface of the nanoparticle. If the platinum nanoparticles are annealed at too high of a temperature, the stabilizing metal atoms may migrate into the bulk or core region of the nanoparticle. In one example, the nanoparticles can be heated between about 100 °C and about 200 °C. In another example, the nanoparticles can be heated to less than or equal to about two times the boiling point of the solvent to be removed. Migration into the bulk of the nanoparticle is also caused by the length of annealing. In one example, the nanoparticles can be heated for about 1 hour or more. In another example, the nanoparticles can be heated for about 1 hour to about 24 hours. The length of annealing is inversely proportional to the annealing temperature. The annealing process should be shorter at higher temperatures to prevent diffusion into the bulk of the nanoparticle. In one specific example, the nanoparticles can be annealed for 24 hours at 100 °C. In another specific example, the nanoparticles can be annealed for 1 hour at 200 °C. Lower temperatures are suggested for smaller platinum particle sizes.

Next, the nanoparticles on the electrode are passivated (step 616). Passivation can include cooling the nanoparticles, such as to ambient temperature, completely replacing the hydrogen atmosphere with an inert gas, and then slowly introducing oxygen into the inert atmosphere so that the inert gas contains about 10% oxygen or less. In one example, the inert gas contains about 3% oxygen or less. In another example, the inert gas contains about 1% oxygen or less. In a further example, the inert gas contains between about 0.1% and about 1% oxygen. It is advisable to limit the temperature rise of the nanoparticles to under about 10 °C on exposure to oxygen containing gas. The inert atmosphere having a low partial pressure of oxygen partially oxidizes the stabilizing metal atoms, and causes one or two oxygen atoms to attach to each deposited stabilizing metal atom. The partial pressure

of oxygen is controlled in order to control the rate of oxidation. Rapid oxidation of the nanoparticles will generate a large amount of heat, which can cause the nanoparticles to glow red and the can decrease or eliminate the catalytic properties of the nanoparticles.

Next, the nanoparticles are mildly annealed in an inert atmosphere to migrate any stabilizing metal atoms deposited on terraces to the edge and corner regions (step 618). Although replacing the removed platinum atoms by depositing the stabilizing metal atoms at the etched locations may be the dominant process, a small amount of stabilizing metal atoms may deposit on the terraces during step 608. The nanoparticles are mildly annealed so that the oxidized stabilizing metal atoms migrate from the terraces to the edge and corner regions of the nanoparticle.

In one example, the annealing atmosphere is at least about 99.999% inert. During step 618, the nanoparticles are gradually warmed to between about 100 °C and about 150 °C. The annealing process causes any partially oxidized stabilizing metal species located on the terraces to diffuse or migrate along the surface of the nanoparticle until it reaches an edge or corner region. The nanoparticle must be mildly annealed to prevent the oxidized stabilizing metal complexes from migrating into the bulk of the nanoparticle. Additionally, the oxygen atoms bonded to the stabilizing metal atoms maintain the stabilizing metal atoms on the surface of the nanoparticle as they migrate, and prevent the stabilizing metal atoms from migrating into the bulk or core region of the nanoparticle. The inert annealing environment is held for an effective period of time. In one example, the atmosphere is held until all the etched edge and corner regions on the nanoparticles are completely covered with oxidized stabilizing metal complexes. In another example, the atmosphere is held for between about 24 and 96 hours. After annealing, the electrode can be fabricated into a membrane electrode assembly (MEA) and used in a fuel cell.

In an optional step, prior to fabricating into a MEA the electrode is introduced to an electrolyte and performance testing is conducted to confirm the formation of oxidized stabilizing metal complexes at the edge and corner regions. In one example, the electrolyte is sulfonic acid. After several hours of operation, the liquid electrolyte can be removed and the electrode containing the stabilized platinum nanoparticles can be fabricated into a membrane electrode assembly (MEA).

The electrolyte in step 604 dissolves the platinum atoms at the edge and corner regions of the nanoparticle into the solution. In step 610 of method 600, the dissolved platinum ions may be recycled to synthesize additional platinum nanoparticles. Alternatively, the platinum ions may be recycled for other uses.

As discussed above, the solution refluxed with the nanoparticles in step 608 must have a concentration of stabilizing metal atoms sufficient to completely cover the locations vacated by the etched platinum atoms. The concentration of the solution can be estimated based upon the atomic fraction of edge and corner atoms on the platinum nanoparticles and the radius of the oxidized stabilizing metal complexes as described above. For example, about 1.9 oxidized Nb complexes, which have an average radius of 0.074 nm in the +4 oxidation state, are required for each etched platinum atom. This estimated amount is the target or minimum concentration of stabilizing metal atoms for the solution. In one example, the solution can contain 20% more than the calculated minimum moles of the stabilizing metal.

FIG. 11 is a schematic of an alternative strong oxide former stabilized nanoparticle 700, which has a cuboctahedron shape, formed by method 600 of FIG. 10. The stabilized nanoparticles described herein may include nanoparticles of any known shape and other examples are shown in the figures and discussed below. Similar to nanoparticle 10, nanoparticle 700 has a core portion and outer surfaces 702, which include terraces 704, edges 706 and corners 708. Similar to nanoparticle 10, core portion of nanoparticle 700 may be formed of platinum, a platinum alloy or at least one non-platinum metal, and terraces 704 are formed of platinum atoms 710. Platinum atoms 710 can be platinum or platinum alloys. Unlike nanoparticle 10, oxidized stabilizing metal complexes 712 are located at edges 706 and corners 708. Each oxidized stabilizing metal complex 712 includes a stabilizing metal atom attached to at least one oxygen atom. The stabilizing metal atoms are selected from the fifth and six rows of groups four through six of the periodic table (zirconium (Zr), niobium (Nb), molybdenum (Mo), hafnium (Hf), tantalum (Ta) and tungsten (W)) and combinations thereof. These transition metals are strong oxide formers, and the oxidized species are not soluble even under strong oxidizing conditions. In contrast, oxidized transition metals from the fourth row of groups four through six of the periodic table (titanium (Ti), vanadium (V) and chromium (Cr)) may have some solubility under strong oxidizing conditions as aquo-ions or in the presence of complexing species. It should be noted that the oxygen atoms are not explicitly shown in oxidized stabilizing metal complexes 712 and oxidized stabilizing metal complexes 712 may be not be drawn to scale.

As shown in FIG. 11, nanoparticle 700, similar to nanoparticle 10 of FIG. 1, has a regular cuboctahedral shape and is essentially free of defects. As such, terraces 704 are formed essentially of all surface atoms. It is more common that nanoparticle 700 would have surface defects and some irregularity in its shape. For example, as described below

and shown in FIG. 12A, terraces 704 may have steps that make each terrace 704 an irregular surface.

FIG. 11 is a schematic of nanoparticle 700 after essentially all the corner and edge regions have been replaced by oxidized stabilizing metal complexes 712. It is recognized that nanoparticle 700 may have a slightly irregular shape due to a difference in size between platinum atoms and oxidized stabilizing metal complexes. Moreover, it is recognized that a minimal amount of oxidized stabilizing metal complexes may attach to the flats of the nanoparticle. However, so long as the nanoparticles are removed from the solution at a predetermined time, in general, the flats of the nanoparticles should remain unchanged. Additionally, mildly annealing the nanoparticles should cause any oxidized stabilizing metal complexes on the terraces or flats to migrate to the edge, corner and surface defect locations.

In one example, the stabilizing metal located on the platinum atoms is niobium (Nb). Although platinum is a noble metal, in operation as catalyst in a fuel cell, platinum atoms on the platinum nanoparticle are unstable and may be oxidized. This causes the platinum atoms to dissolve from the nanoparticle, resulting in an unstable platinum catalyst. The oxidized cyclopentadiene of niobium is well suited for use in a fuel cell because the oxidized complex stabilizes the adjoining nanocrystallite surfaces and is insoluble in acid. By locating the oxidized complexes at the edges and corners of the nanoparticle, the edges and corners of the nanoparticle do not dissolve during operation of the fuel cell and the catalyst remains stable over time.

Moreover, if only the corners and edge regions of the nanoparticle are covered with the oxidized stabilizing metal complexes, the impact on the ORR activity of the platinum catalyst is negligible. As shown in FIG. 11, oxidized stabilizing metal complexes 712 essentially completely replace the edge and corner regions of nanoparticle 700. In FIG. 11, nanoparticle 700 is large enough such that the majority of the total surface area of nanoparticle 700 is still formed by platinum atoms 710. For smaller sized nanoparticles, which have less platinum atoms on each terrace or flat, the oxidized stabilizing metal complexes that form the edge and corner regions occupy a greater portion of the total surface area of the nanoparticle. As mentioned above, in one example, a suitable range of the diameter of the platinum nanoparticles is between approximately 1 and 20 nm; in another example, the diameter ranges between approximately 1 and 10 nm. For smaller-sized nanoparticles (i.e. less than 1.5 nm), the oxidized stabilizing metal complexes occupy more of the surface area of the nanoparticle. As such, the oxidized stabilizing metal

complexes may occupy up to approximately seventy-five percent of the total surface area of the nanoparticle. On the other hand, nanoparticles up to or greater than 10 nanometers may also be used, and thus the oxidized stabilizing metal complexes may occupy as little as approximately five percent of the total surface area. Therefore, the oxidized stabilizing metal complexes may occupy between approximately five and approximately seventy-five percent of a total surface area of the nanoparticle.

Nanoparticles 700 described herein use less platinum compared to nanoparticle 10 of FIG. 1 because the platinum atoms on the nanoparticles are removed and replaced with a stabilizing metal. The replaced platinum may then be recycled. Platinum atoms are selectively removed and replaced with niobium (or another stabilizing metal) at the corners and edges, as well as at any surface defects. Because the stabilizing metal atoms only cover the corners and edges, and any surface defects, the nanoparticles maintain their catalytic activity, but are more durable during potential cycling.

Nanoparticles 700 shown thus far have had regular cuboctahedron shapes and have been essentially free of defects. As such, terraces 704 of nanoparticles 700 have been shown as flat surfaces comprised essentially of all surface atoms. In reality, the nanoparticles described herein commonly have surface defects that form as a result of the synthesis process used in forming the nanoparticles. FIG. 12A is a schematic of an enlarged portion of one of terraces 704 from nanoparticle 700 of FIG. 11 to illustrate these surface defects. Terrace 704 of FIG. 11 is a (111) surface, and thus is referred to as Pt (111) terrace 704. FIGS. 12A and 12B illustrate that, if these surface defects are present on a nanoparticle, the surface defect platinum atoms will be etched or removed from the nanoparticle by dissolution and oxidized atoms from a stabilizing metal from the fifth and sixth rows of groups four through six of the periodic table will deposit at these surface defect sites due to the similar reactivity of edge sites and surface defect sites. (Note that the surface defects shown in FIG. 12A are not visible in FIG. 11.)

As shown in FIG. 12A, Pt (111) terrace 704 is formed of all platinum atoms 710 and includes stable portion 704a and ledge 714. Step 714 is a layer of platinum atoms 710 that forms over part of stable portion 704a, resulting in an elevated layer of atoms 710. Similar to atoms 710 on stable portion 704a, the majority of atoms 710 on ledge 714 are surface atoms. Because platinum has a face-centered cubic unit cell, a surface atom on a (111) surface has nine nearest neighbor atoms. The stability of each atom is a function, in part, of how many other atoms are surrounding that atom. Like the surface atoms in stable portion 704a, most atoms on ledge 714 have nine nearest neighbor atoms. However, platinum

atoms 710 located in a last row of ledge 714 (labeled as 714a) are more reactive because these atoms have no more than seven nearest neighbor atoms. More specifically, last row 712a includes step atoms 716, kink atom 718 and step adatom 720. Step atoms 716 are defined as atoms having seven nearest neighbor atoms. Kink atom 718 has six nearest
5 neighbor atoms, including a step atom 716. Finally, step adatom 720 has only five nearest neighbor atoms. It is recognized that the nearest neighbor atoms for surface atoms, step atoms, kink atoms and step adatoms may vary based on the crystallographic orientation of the facet surface.

FIG. 12A shows terrace 704 before removal and replacement of platinum atoms.
10 FIG. 12B shows terrace 704 after selectively etching platinum atoms of last row 714a of ledge 714. As described above, platinum atoms are removed or etched from the nanoparticles. Dissolution of atoms at edges, corners and surface defect is more favorable compared to atoms at the flats or terraces due to the decreased stability of these atoms having a smaller number of nearest neighbors. Therefore, platinum atoms at the edges,
15 corners and surface defects are etched first. The etching process is stopped after the platinum atoms at the edges, corners and surface defects are removed but before platinum atoms on the terraced are removed. After etching, atoms from a stabilizing metal are deposited on the nanoparticles and are oxidized. The most reactive sites on the nanoparticles will be where the platinum atoms were removed due to the reduced number of
20 nearest atoms at these locations. This is where the stabilizing metal atoms will deposit.

FIG. 12C shows Pt (111) terrace 704 after oxidized stabilizing metal atoms 712 are deposited on the nanoparticle. As shown in Pt (111), platinum atoms 710 at the surface defects are removed and are replaced by oxidized stabilizing metal atoms 712. It is recognized that multiple steps may be present on terrace 704, including multiple steps on
25 top of one another. The nanoparticles described herein may vary in terms of amount of surface defects present on the nanoparticles.

As described above, the platinum nanoparticles are removed from the dissolution or etching conditions after a time sufficient such that the terraces, which are the less-reactive regions of the nanoparticles, remain unchanged. More specifically, the platinum surface
30 atoms on the terraces are not removed. By contrast, the atoms that form the steps and kinks on the terraces may likely be removed during etching, because these atoms are more reactive than surface atoms on the terraces. Unless a nanoparticle has an unusually large number of surface defects, the majority of the terraces should remain unchanged so long as the nanoparticles are removed from the solution after a time determined sufficient to only

remove the platinum atoms at the reactive sites on the nanoparticle. Depending on an amount of surface defects, the oxidized stabilizing metal complexes may occupy a greater percentage of the surface area of the nanoparticle than the ranges provided above, which were based on the edge and corner regions of the nanoparticle.

5 FIG. 13 is a schematic of stabilized nanoparticle 800, which is similar to stabilized nanoparticle 700 of FIG. 11, but is cubic-shaped. Nanoparticle 800 has a core formed of platinum, a platinum alloy or at least one other transition metal. Outer surfaces 802 of nanoparticle 800 are formed of platinum atoms 804 on flats or terraces 806, and oxidized stabilizing metal complexes 810 on edges 808 and corners 809. Nanoparticle 800, as shown
10 in FIG. 13, has a regular cubic shape, and terraces 806 are generally free of defects. However, as described above, it is recognized that nanoparticle 800 may have surface defects or features that result in nanoparticle 800 having an irregular shape and terraces 806 having uneven surfaces. Stabilized nanoparticle 800 has already undergone method 500 of FIG. 10 so that terraces 806 are primarily formed of platinum atoms 804 and edges 808 and
15 corners 809 are formed of oxidized stabilizing metal complexes 810.

As described above, an unstabilized platinum or platinum alloy nanoparticle primarily has platinum atoms on all outer surfaces 802. The unstabilized nanoparticle is etched to remove platinum atoms 804 from edges 808 and corners 809, which are more reactive than terraces 806. The etching conditions are applied to the nanoparticle for a
20 specified time so that platinum atoms 804 are only removed from edges 808 and corners 809. After removing platinum atoms 804 from edges 808 and corners 809, the nanoparticle is combined with a solution containing compounds of a stabilizing metal from the fifth and sixth rows of groups four through six of the periodic table (zirconium, niobium, molybdenum, hafnium, tantalum and tungsten). As described above, the compounds
25 deposit stabilizing metal atoms on the nanoparticle. The stabilizing metal atoms will deposit at the etched locations, due to the increased reactivity of these locations. After deposition, the stabilizing metal atoms are partially oxidized to form oxidized stabilizing metal complexes 810, and the nanoparticle may be mildly annealed to migrate any oxidized stabilizing metal complexes 810 on terraces 806 to edges 808 and corners 809. The result is
30 stabilized nanoparticle 800, having oxidized stabilizing metal complexes 810 located at edges 808 and 809.

As described above, oxidized stabilizing metal complexes 810 are smaller in size than platinum atoms, although FIG. 13 is not to scale. An overall size of nanoparticle 800 remains unchanged compared to the original unstabilized nanoparticle, particularly since the

stabilizing metal atoms are deposited in an amount sufficient to replace the etched platinum atoms at the edges and corners. It is recognized that nanoparticle 800 may have a slightly irregular shape compared to the unstabilized nanoparticle; however, nanoparticle 800 remains generally cubic-shaped.

Although not shown in FIG. 13, it is recognized that nanoparticle 800 may commonly include surface defects, such as steps and kinks, on terraces 806. The platinum atoms that form the steps and kinks have reactivities similar to the reactivities of platinum atoms at edges 808 and corners 809. As such, the platinum atoms at the steps and kinks may also be removed and replaced with oxidized stabilizing metal complexes.

FIG. 14 is a schematic of stabilized nanoparticle 850, similar to nanoparticles 700 and 800, but having a tetrahedron shape. Nanoparticle 850 is formed of a core portion and outer surfaces 852. Outer surfaces 852 are formed of platinum atoms 854 and include terraces 856, edges 858 and corners 859. It is recognized that nanoparticle 850, in reality, may have a more irregular tetrahedron-based shape, and that surface defects (i.e. steps and kinks) may be present on terraces 856. As illustrated in FIG. 14, stabilized nanoparticle 850 has already undergone process 500 of FIG. 10 so that platinum atoms 854 at edges 858 and corners 859 have been removed and replaced with oxidized stabilizing metal complexes 860.

As discussed above, when a nanoparticle is subjected to etching conditions, platinum atoms 854 at edges 858 and corners 859 are removed. The etched nanoparticle is then combined with stabilizing metal compounds in a solution. The stabilizing metal compounds contain transition metal atoms selected from the fifth and sixth rows of groups four through six of the periodic table (zirconium (Zr), niobium (Nb), molybdenum (Mo), hafnium (Hf), tantalum (Ta) and tungsten (W)). The stabilizing metal atoms are deposited at corners 858 and edges 859 where platinum atoms 854 have been removed due to the higher reactivity of these sites on the nanoparticle. Following deposition, the stabilizing metal atoms are partially oxidized to form oxidized stabilizing metal complexes 860.

FIG. 14 shows stabilized nanoparticle 850 with oxidized stabilizing metal complexes 860 located at edges 858 and corners 859. Oxidized stabilizing metal complexes 860 have essentially replaced all of platinum atoms 854 at edge and corner regions 858 and 859. Stabilized nanoparticle 850 may have a slightly irregular shape due to a difference in size between platinum atoms 854 and oxidized stabilizing metal complexes 860. Since nanoparticle 850 may have surface defects on terraces 856, it is recognized that nanoparticle 850 may also include oxidized stabilizing metal complexes 860 on terraces 856 where

oxidized stabilizing metal complexes 860 have replaced platinum step atoms, kink atoms and step adatoms forming a surface defect.

Platinum nanoparticles are commonly used as an electrocatalyst in an electrochemical cell, and the stabilized platinum nanoparticles described herein may result in a more active catalyst. FIG. 15 is one example of fuel cell 900, which includes the platinum nanoparticles described herein as a stabilized cathode catalyst layer.

Fuel cell 900 is designed for generating electrical energy and includes anode 902, anode catalyst layer 904, electrolyte 906, cathode 908, and cathode catalyst layer 910. Anode 902 includes flow field 912 and cathode 908 includes flow field 914. In one example, fuel cell 900 is a hydrogen cell using hydrogen as fuel and oxygen as oxidant. It is recognized that other types of fuels and oxidants may be used in fuel cell 900.

Anode 902 receives hydrogen gas (H_2) by way of flow field 912. Catalyst layer 904, which may be a platinum catalyst, causes the hydrogen molecules to split into protons (H^+) and electrons (e^-). Electrolyte 906 allows the protons to pass through to cathode 908, but the electrons are forced to travel to external circuit 916, resulting in a production of electrical power. Air or pure oxygen (O_2) is supplied to cathode 908 through flow field 914. At cathode catalyst layer 910, oxygen molecules react with the protons from anode 902 to form water (H_2O), which then exits fuel cell 900, along with excess heat.

Anode catalyst layer 904 and cathode catalyst layer 910 may each be formed from platinum nanoparticles. As described above, cathode catalyst layer 910 is used to increase the rate of the oxygen reduction reaction (ORR) causing the formation of water from protons and oxygen. Even though platinum is a catalytic material, the platinum is unstable in this environment. During potential cycling, platinum atoms from the platinum nanoparticles dissolve, particularly starting from corner and edge regions of the nanoparticles. Platinum nanoparticles 100, 700 described herein and shown in FIGS. 2 and 11 are more stable nanoparticles and are more durable for use as cathode catalyst layer 910. It is recognized that the nanoparticle of the present invention may also be used for anode catalyst layer 904. However, the platinum is more stable in the environment used for anode catalyst layer 904, and the problems described above for cathode catalyst layer 910 do not generally apply to layer 904.

In one example, fuel cell 900 is a polymer electrolyte membrane (PEM) fuel cell, in which case electrolyte 906 is a proton exchange membrane formed from a solid polymer. In another example, fuel cell 900 is a phosphoric acid fuel cell, and electrolyte 906 is liquid phosphoric acid, which is typically held within a ceramic matrix. Cubo-octahedral shaped

nanoparticles, like nanoparticle 10 of FIG. 1, are commonly used in fuel cells, including PEM and phosphoric acid fuel cells. Other nanoparticle shapes that have been studied for use as platinum catalysts include, but are not limited to, cubic and tetrahedral nanoparticles. Specific shaped nanoparticles may be more stable in a specific type of electrolyte.

5 It is recognized that a platinum catalyst may use nanoparticles having a variety of shapes and it is not required that a particular shape be used with a particular fuel cell. However, the ORR activity may be influenced, in part, by a combination of the type of electrolyte and the shape of the nanoparticles. This may be due to a difference in the crystal faces that form the shapes of the nanoparticles. Cubic nanoparticles are formed essentially
10 of all (100) surfaces, whereas tetrahedral nanoparticles are formed of (111) surfaces.

In some examples, the cathode catalyst for a phosphoric acid fuel cell is formed of cubic-shaped platinum nanoparticles having corner and edge regions formed of a stabilizing metal (see FIGS. 8A and 13). If the cubic nanoparticles include a stabilizing metal, such as niobium, the cathode catalyst is more stable, and thus should have a longer operational life
15 since a total mass of the cathode catalyst should remain relatively constant. On the other hand, in a PEM fuel cell, the cathode catalyst, in some examples, is formed of tetrahedral-shaped platinum nanoparticles having corner and edge regions formed of a stabilizing metal (see FIGS. 9A and 14). By using a tetrahedral-shaped nanoparticle having oxidized stabilizing metal complexes located at the corners and edges, the ORR activity of the
20 nanoparticles in the PEM fuel cell may be further increased. It is recognized that, in either a PEM or a phosphoric acid fuel cell, the catalyst may also include nanoparticles of at least one other shape.

It is also recognized that a platinum catalyst may use nanoparticles having a variety of shapes and it is not required that a particular shape be used with a particular fuel cell.
25 For example, the platinum catalyst can be cubic-shaped nanoparticles having stabilizing metal atoms located at the edge, corner and surface defect sites. In another example, the platinum catalyst can be tetrahedron-shaped nanoparticles having stabilizing metal atoms located at the edge, corner and surface defect sites. It is also recognized that, in either a PEM or a phosphoric acid fuel cell, the catalyst can also include nanoparticles of at least
30 one other shape.

The present disclosure of forming a more stable platinum nanoparticle applies to all nanoparticles, regardless of shape. Although specific shapes (i.e. cubo-octahedral, cubic and tetrahedral) are described above and illustrated in the figures, it is recognized that nanoparticles having additional shapes are within the scope of the present disclosure. Other

nanoparticle shapes include, but are not limited to, icosahedral, rhombohedral, and other types of polyhedrons. Additional nanoparticle shapes include cylindrical, spherical, and quasi-spherical, which do not have well-defined edge and corner regions. The atoms that form the defects, steps and kinks on these nanoparticles are believed to have similar reactivity to edge and corner atoms, and oxidized stabilizing metal complexes may consequently favor these locations.

Further, although the PtO dissolution enthalpies presented in Table 2 are for (111)x(111) edges and (111) terraces, similar trends are seen for other edges and terraces. The selective population of strong oxide former transition metals (Zr, Hf, Nb, Ta, Mo and W) will also have a stabilizing effect on nanoparticles having surfaces other than (111) surfaces.

Although the stabilized platinum nanoparticles of the present disclosure are described in the context of use as a catalyst in a fuel cell, the nanoparticles may also be used in other types of electrochemical cells, including but not limited to, batteries and electrolysis cells. The nanoparticles may also be used in other applications that would benefit from platinum nanoparticles have a more stable structure, including other catalyst applications, as well as non-catalyst applications.

Although the present invention has been described with reference to preferred embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

CLAIMS:

1. A nanoparticle having a core portion surrounded by a plurality of outer surfaces, the nanoparticle comprising:

a plurality of platinum atoms that form a plurality of terraces on the nanoparticle;

and

a plurality of atoms from a stabilizing metal located at edge regions and corner regions of the nanoparticle, wherein the outer surfaces of the nanoparticle include the terraces, the edge regions, and the corner regions, and wherein the stabilizing metal includes at least one of zirconium, niobium, molybdenum, hafnium, tantalum and tungsten.

2. The nanoparticle of claim 1 wherein the outer surfaces of the nanoparticle further include surface defects on the terraces, and atoms from the stabilizing metal are located at the surface defects.

3. The nanoparticle of claim 2 wherein the surface defects include at least one of a step atom, a kink atom, and a step adatom.

4. The nanoparticle of claim 1 wherein the nanoparticle is selected from a group consisting of cubic nanoparticles, cubo-octahedral nanoparticles, tetrahedral nanoparticles, icosahedral nanoparticles, spherical nanoparticles, quasi-spherical nanoparticles, rhombohedral nanoparticles, and truncated octahedral nanoparticles.

5. The nanoparticle of claim 1, wherein the stabilizing metal atoms are oxidized.

6. The nanoparticle of claim 1 wherein the stabilizing metal atoms occupy between approximately 5 and approximately 75 percent of a total surface area of the outer surfaces of the nanoparticle.

7. The nanoparticle of claim 1 wherein the core portion of the nanoparticle is formed of at least one of platinum, a platinum alloy, and a transition metal selected from a group consisting of transition metals from a fourth, fifth, and sixth row of the periodic table.

8. The nanoparticle of claim 1 wherein the nanoparticle is a catalyst in an electrochemical cell.

9. A nanoparticle comprising:

a core formed of at least one of platinum, a platinum alloy and a transition metal selected from a group consisting of transition metals from a fourth, fifth and sixth row of the periodic table;

a plurality of adjoining terraces, wherein each terrace is formed of platinum surface atoms;

a plurality of edge regions having atoms from a stabilizing metal, wherein each edge region is an intersection between two adjoining terraces; and

a plurality of corner regions having atoms from the stabilizing metal and defining an intersection of at least two edge regions, wherein the stabilizing metal includes at least one of zirconium, niobium, molybdenum, hafnium, tantalum and tungsten.

10. The nanoparticle of claim 9 wherein each terrace includes surface defects having atoms from the stabilizing metal.

11. The nanoparticle of claim 9 wherein the surface defects include at least one of a step atom, a kink atom, and a step adatom.

12. The nanoparticle of claim 9 wherein the atoms from the stabilizing metal occupy between approximately 5 and approximately 75 percent of a total surface area of an outer surface of the nanoparticle.

13. The nanoparticle of claim 9, and further comprising an oxygen atom attached to each atom from the stabilizing metal.

14. The nanoparticle of claim 9 wherein a shape of the nanoparticle includes at least one of cubic, tetrahedral, cubo-octahedral, icosahedral, spherical, quasi-spherical, rhombohedral, and truncated octahedral.

15. The nanoparticle of claim 9 wherein a diameter of the nanoparticle is between approximately 0.5 and approximately 100 nanometers.

16. The nanoparticle of claim 9 wherein a diameter of the nanoparticle is between approximately 1 and 20 nanometers.

17. A stabilized platinum catalyst comprising:

a plurality of nanoparticles, wherein each nanoparticle comprises:

a core formed of at least one of platinum, a platinum alloy and a transition metal selected from a group consisting of transition metals from a fourth, fifth and sixth row of the periodic table;

a plurality of adjoining terraces formed of platinum surface atoms;

a plurality of edge regions having atoms from a stabilizing metal, wherein each edge region is an intersection of two terraces; and

a plurality of corner regions having atoms from the stabilizing metal, wherein each corner region is an intersection of at least two edge regions, and wherein the stabilizing metal includes at least one of zirconium, niobium, molybdenum, hafnium, tantalum and tungsten.

18. The stabilized platinum catalyst of claim 17 wherein each terrace includes at least one of a step atom, a kink atom and a step adatom formed from the stabilizing metal.

19. The stabilized platinum catalyst of claim 17, and further comprising at least one oxygen atom attached to each stabilizing metal atom.

20. The stabilized platinum catalyst of claim 17 wherein the nanoparticles include at least one of cubic nanoparticles, tetrahedral nanoparticles, cuboctahedral nanoparticles, icosahedral nanoparticles, spherical nanoparticles, quasi-spherical nanoparticles, rhombohedral nanoparticles, and truncated octahedral nanoparticles.

21. The stabilized platinum catalyst of claim 17 wherein the nanoparticles are supported on a substrate.

22. The stabilized platinum catalyst of claim 21 wherein the substrate includes at least one of carbon black, modified carbon black, metal oxides, metal carbides and boron doped diamond.

23. The stabilized platinum catalyst of claim 17 wherein the catalyst is an electrocatalyst in an electrochemical cell.

24. The stabilized platinum catalyst of claim 23 wherein the electrochemical cell includes at least one of a fuel cell, a battery, and an electrolysis cell.

25. The stabilized platinum catalyst of claim 24 wherein the fuel cell is selected from a group consisting of a phosphoric acid fuel cell and a proton exchange membrane (PEM) fuel cell.

26. The stabilized platinum catalyst of claim 21 wherein the stabilizing metal atoms occupy between approximately 5 and approximately 75 percent of a total surface area of an outer surface of the nanoparticle.

27. The stabilized platinum catalyst of claim 21 wherein a diameter of the nanoparticle is between approximately 0.5 and 100 nanometers.

28. The stabilized platinum catalyst of claim 21 wherein a diameter of the nanoparticle is between approximately 1 and 20 nanometers.

29. A method of producing a stabilized platinum nanoparticle, the method comprising: depositing atoms from a stabilizing metal onto a platinum nanoparticle; and

annealing the nanoparticle so that the atoms from the stabilizing metal remain on the surface of the nanoparticle, wherein the stabilizing metal includes at least one of zirconium, niobium, molybdenum, hafnium, tantalum and tungsten.

30. The method of claim 29, and further comprising oxidizing the deposited atoms from the stabilizing metal.

31. The method of claim 30, wherein oxidizing comprises exposing the deposited atoms from the stabilizing metal to an inert atmosphere containing less than about 10% oxygen.

32. The method of claim 30 wherein annealing the nanoparticles comprises heating the nanoparticles between about 100 °C and about 150°C.

5 33. The method of claim 29, wherein depositing stabilizing metal atoms comprises:
etching the platinum nanoparticles to remove platinum atoms from edge and corner regions;
adding a solution of low or zero valent compounds to the etched nanoparticles,
wherein low or zero valent compounds include atoms from the stabilizing
10 metal; and
replacing the removed platinum atoms with the atoms from the stabilizing metal.

34. The method of claim 33, wherein the low or zero valent compounds are selected from the group consisting of: $[M(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ where M is Zr or Hf, $[M(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_4]$ where M is Nb or Ta, molybdenum carbonyl $[(\text{Mo}(\text{CO})_6)]$, tungsten carbonyl, $[\text{W}(\text{CO})_6]$ and
15 mixtures thereof.

35. The method of claim 29, wherein depositing atoms of the stabilizing metal comprises:

creating a suspension containing platinum nanoparticles;
flushing the suspension with hydrogen;
20 adding a solution of low or zero valent compounds to the suspension, wherein the
low or zero valent compounds include atoms from the stabilizing metal; and
refluxing the suspension after addition of the solution.

36. The method of claim 35, wherein the low or zero valent compounds are selected from the group consisting of: $[M(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ where M is Zr or Hf, $[M(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_4]$
25 where M is Nb or Ta, molybdenum carbonyl $[(\text{Mo}(\text{CO})_6)]$, tungsten carbonyl, $[\text{W}(\text{CO})_6]$, and
mixtures thereof.

1/16

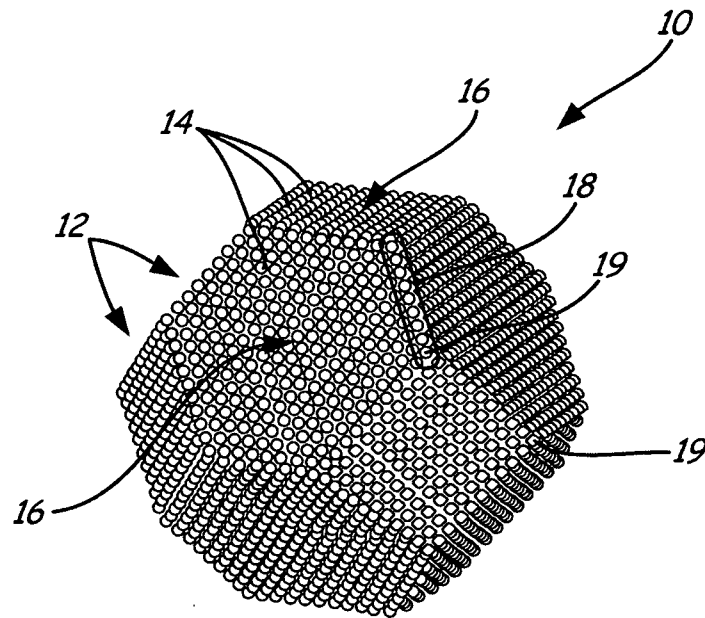


FIG. 1
(PRIOR ART)

2/16

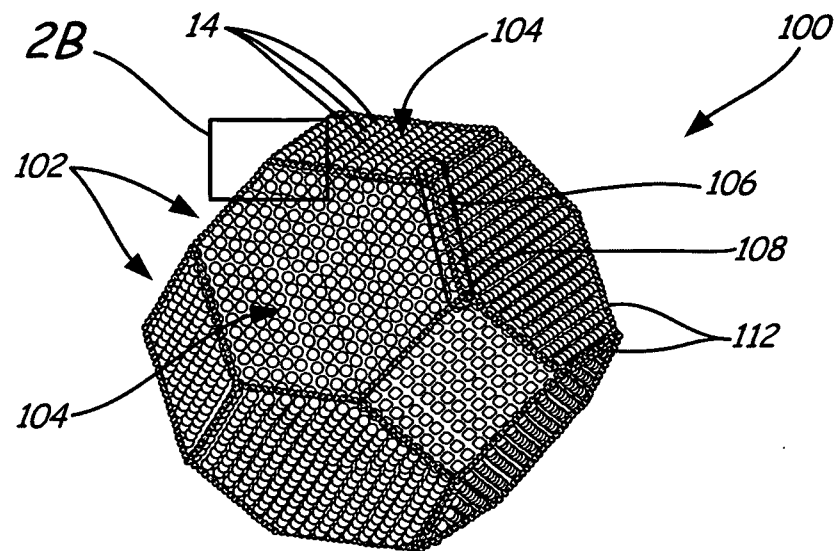
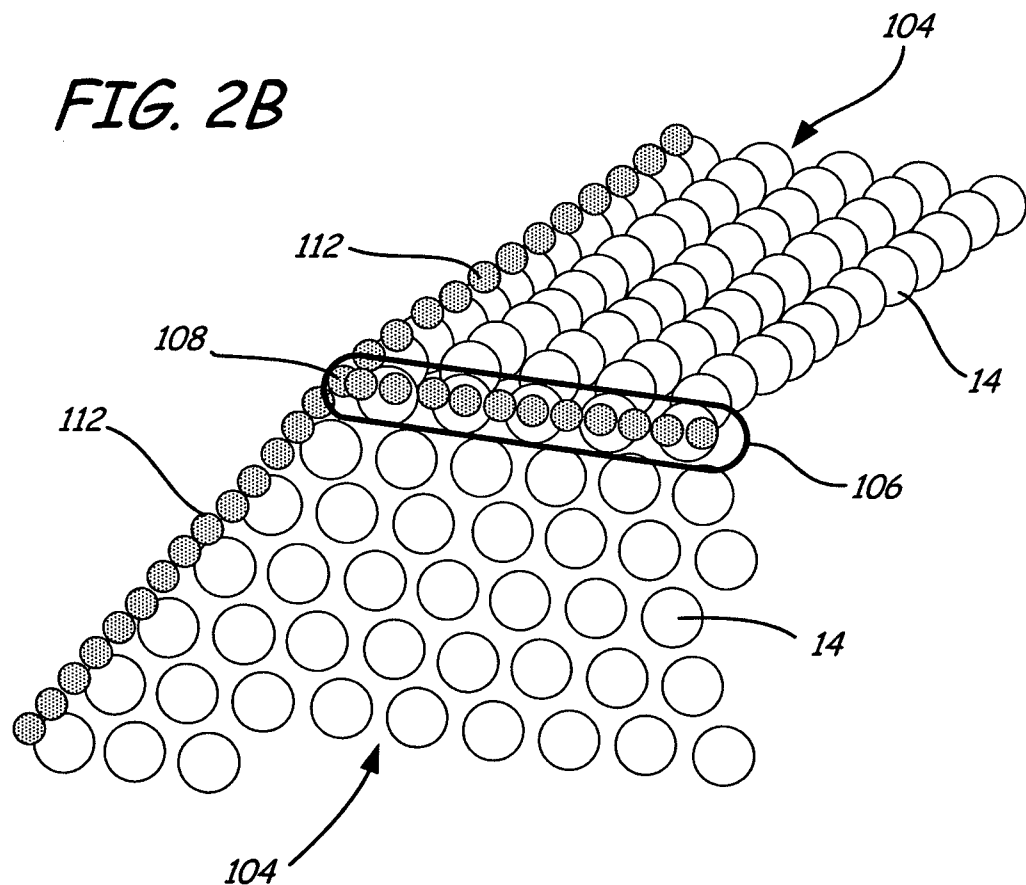


FIG. 2A



3/16

200

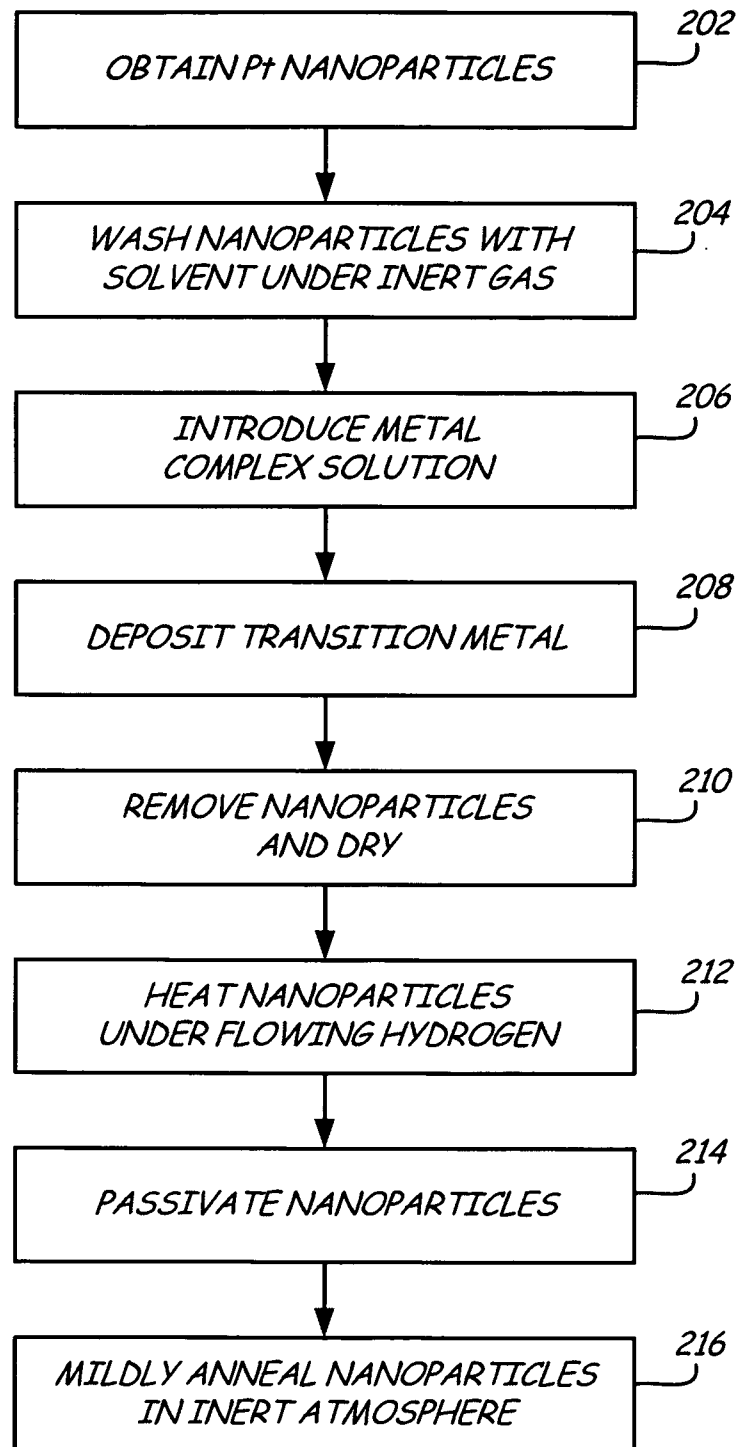


FIG. 3

SUBSTITUENT OXIDATIVE MIGRATION TO DIFFERENT POSITIONS
AFTER DEPOSITION AT EDGE FROM SOLUTION

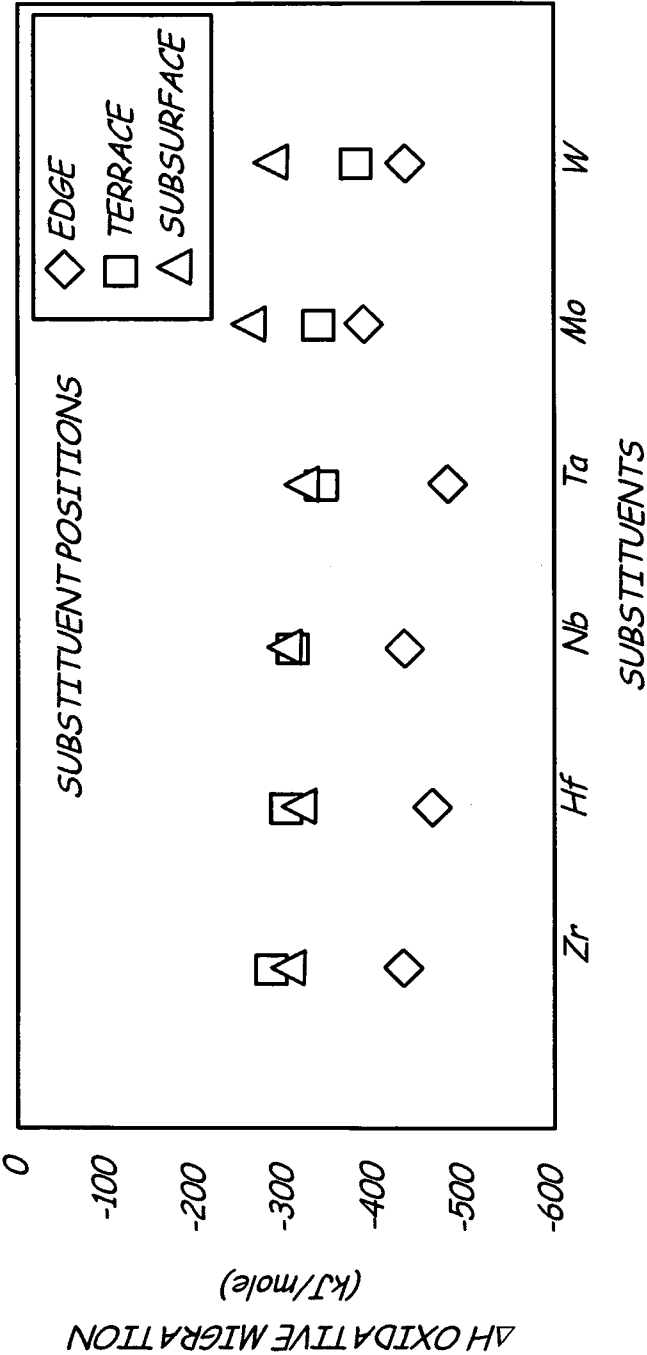


FIG. 4

SUBSTITUENT OXIDATIVE MIGRATION TO DIFFERENT POSITIONS
AFTER DEPOSITION AT FACE FROM SOLUTION

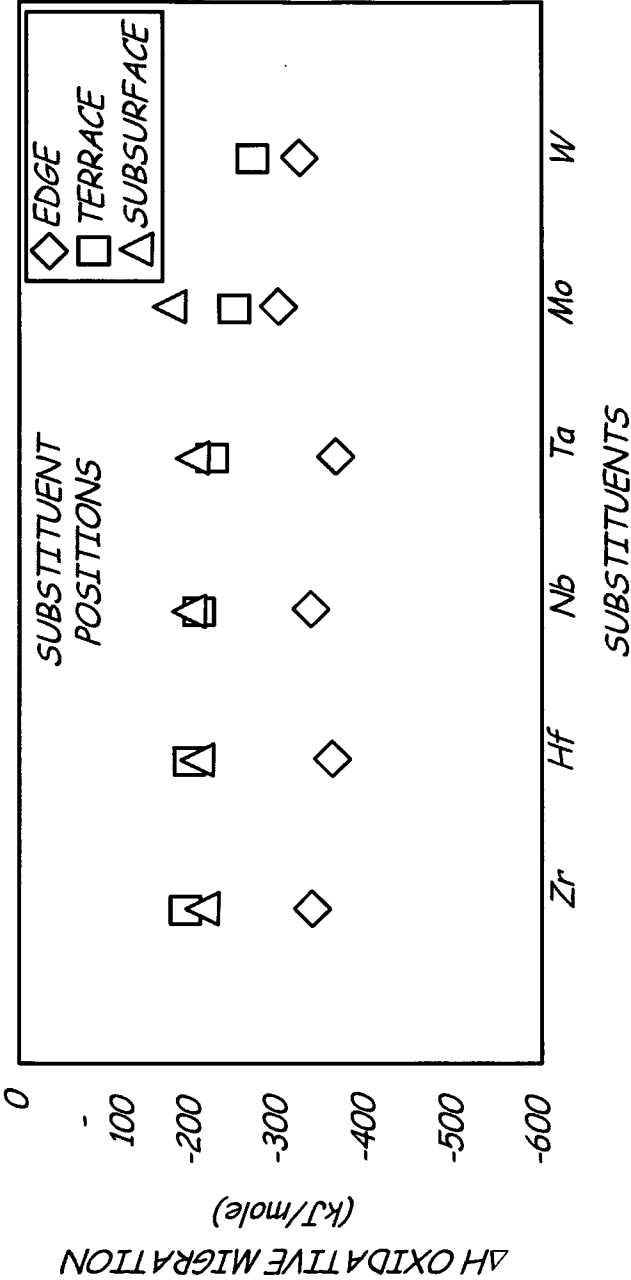
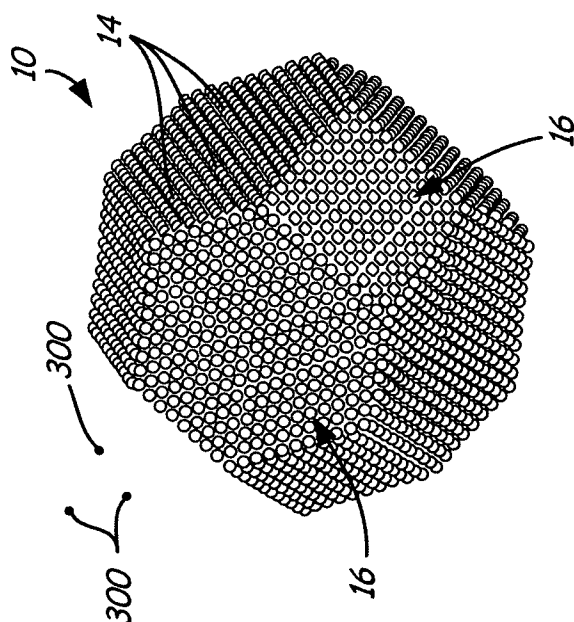
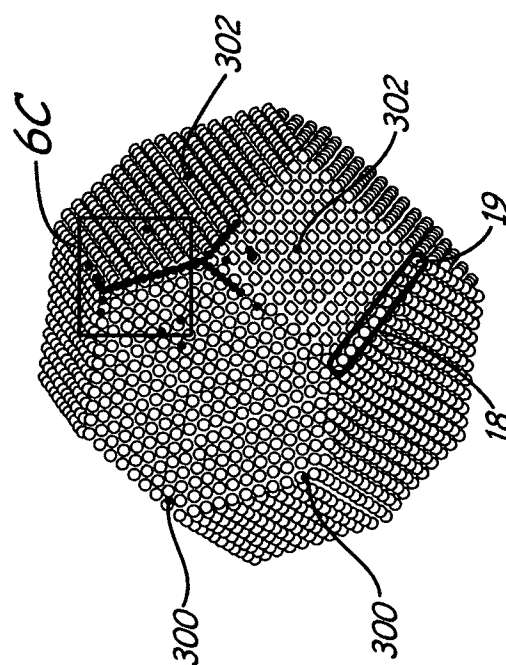
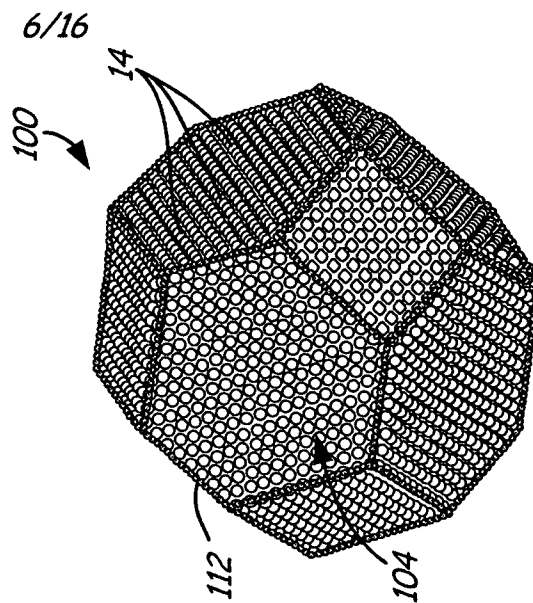
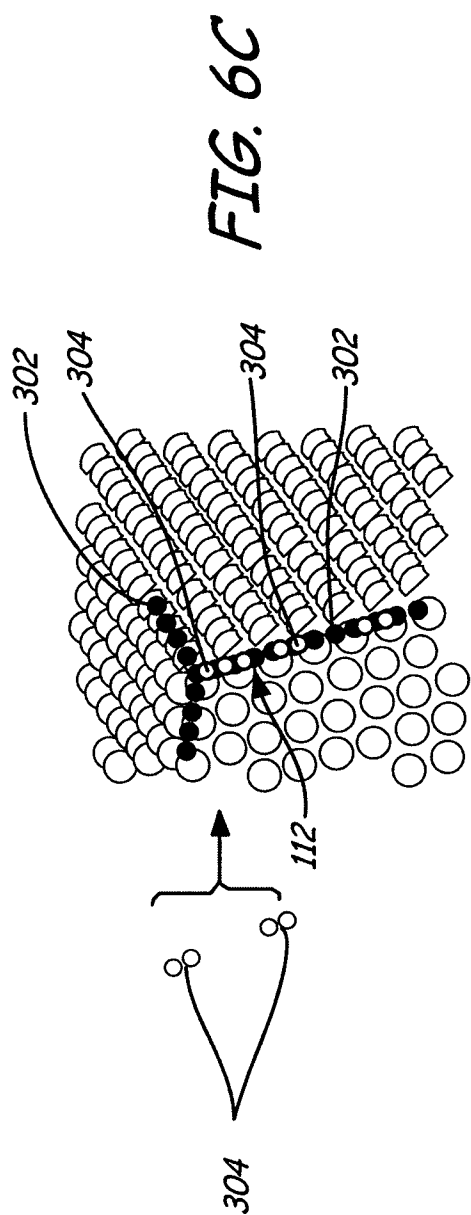
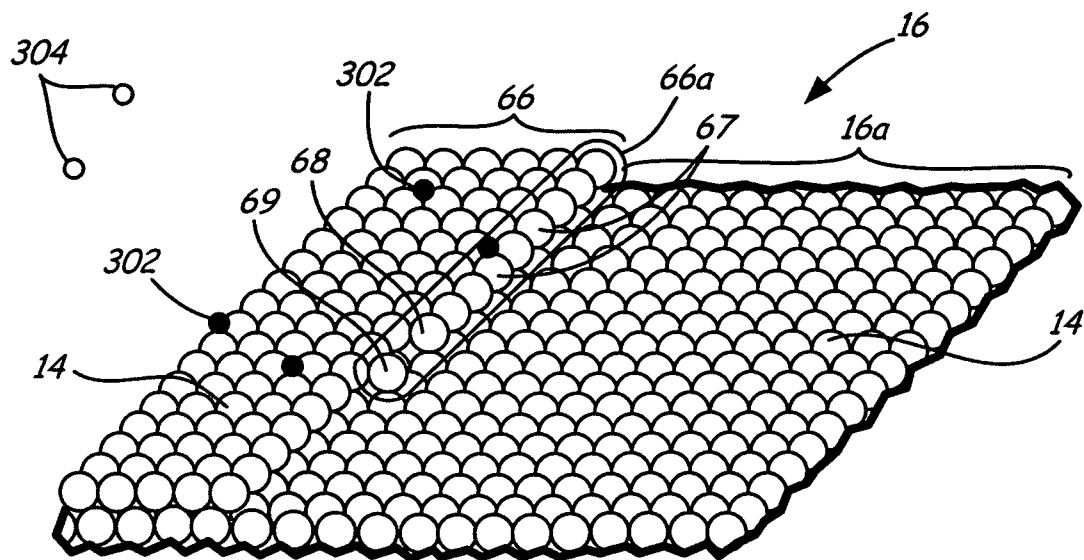
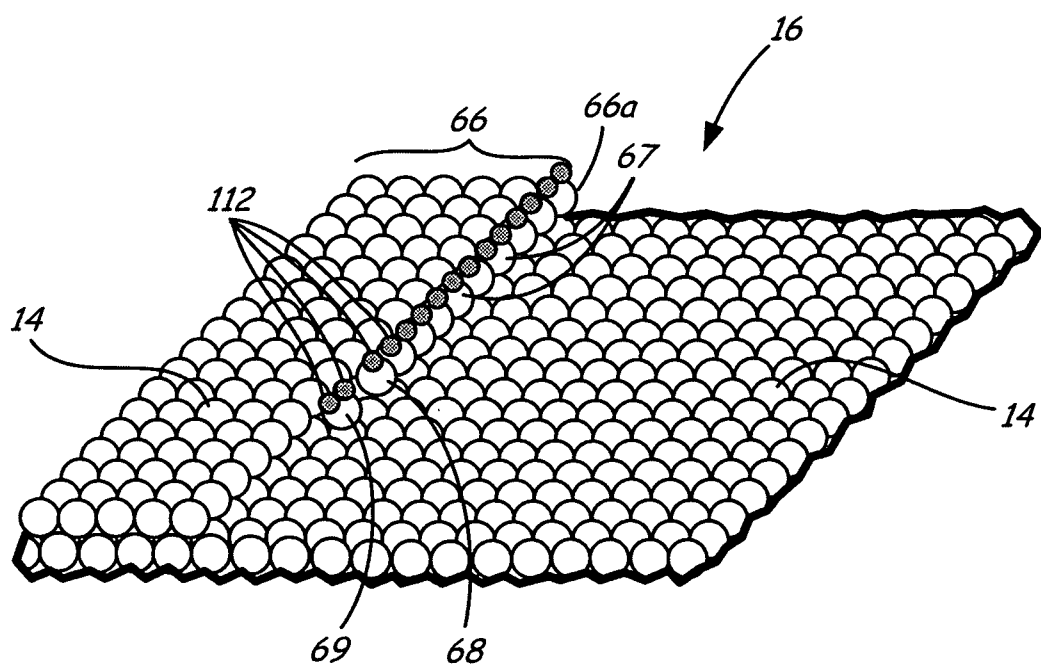


FIG. 5



7/16

*FIG. 7A**FIG. 7B*

8/16

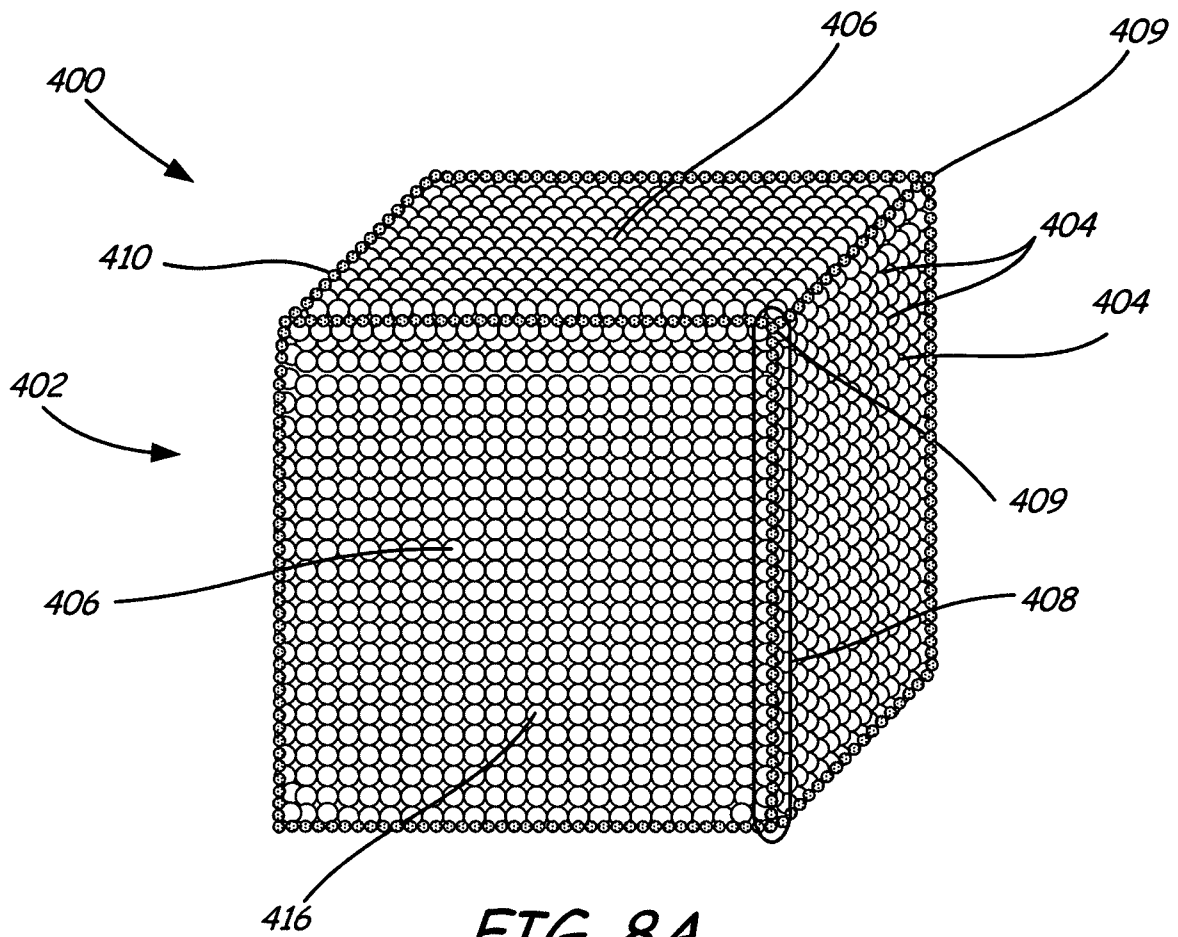


FIG. 8A

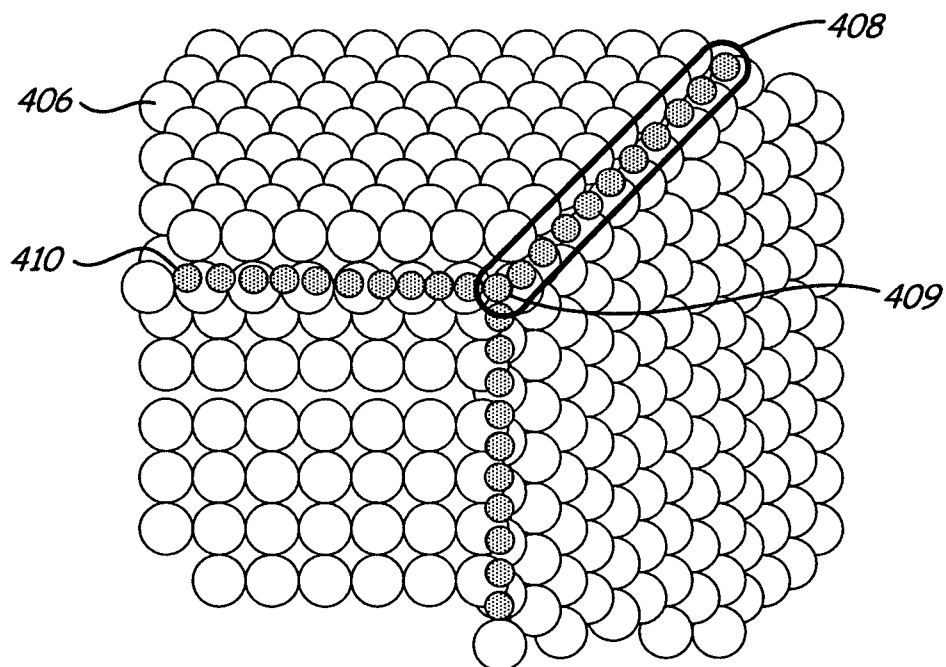


FIG. 8B

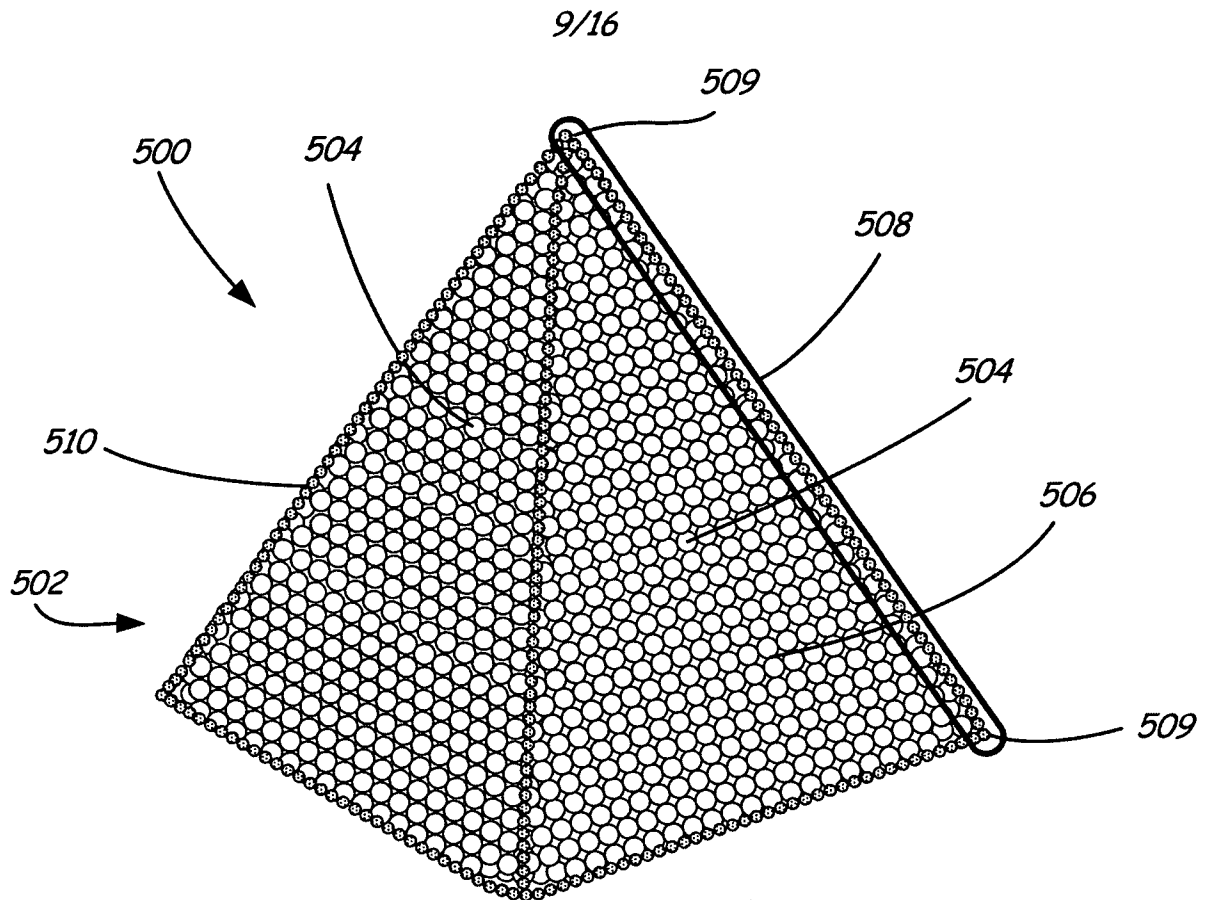


FIG. 9A

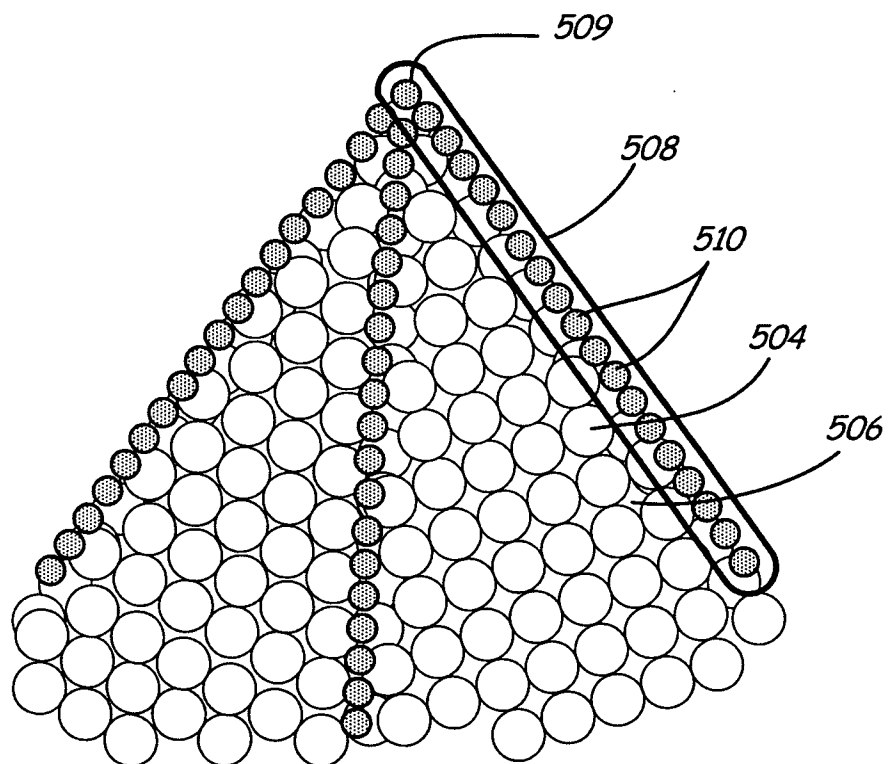


FIG. 9B

10/16

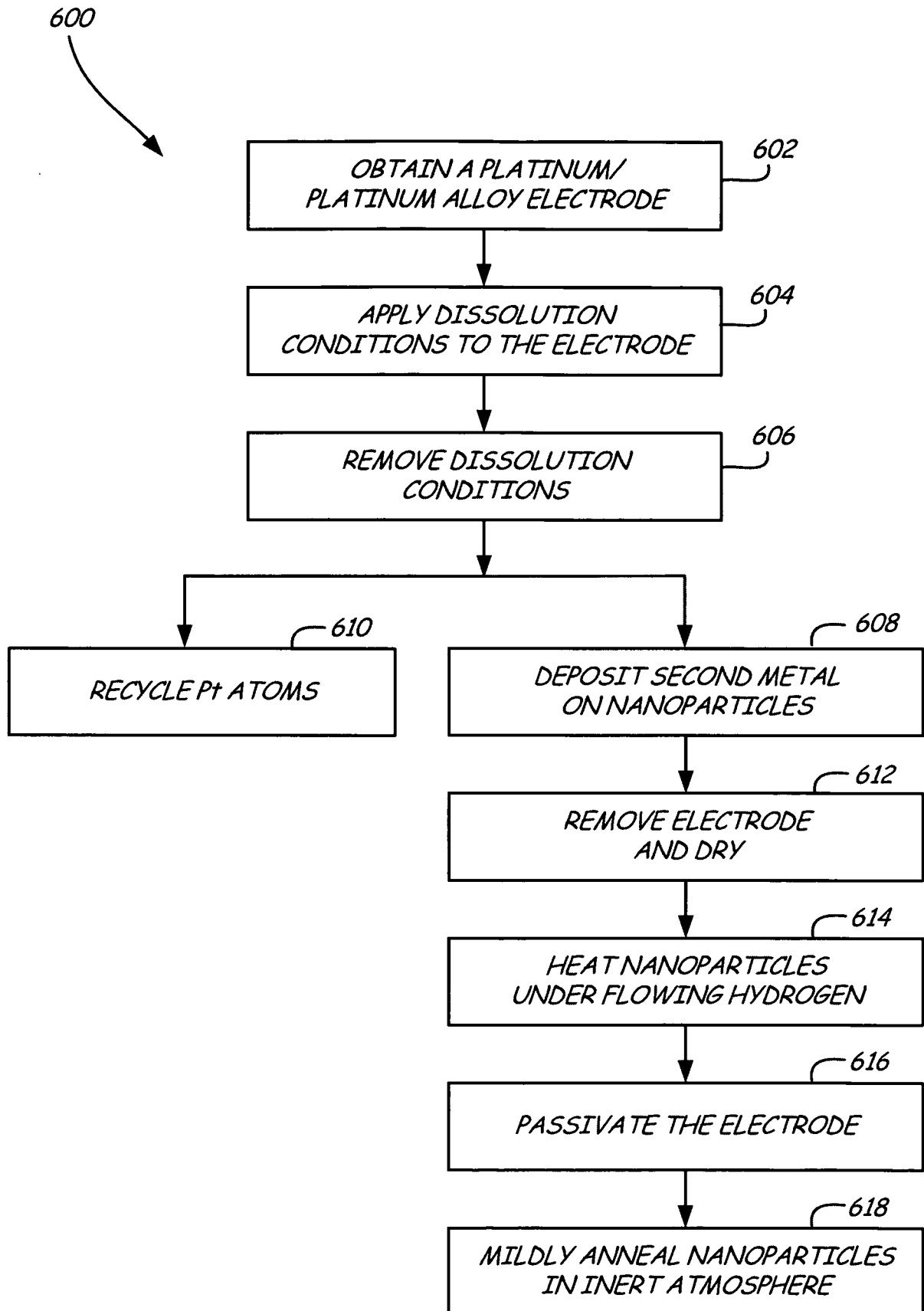


FIG. 10

11/16

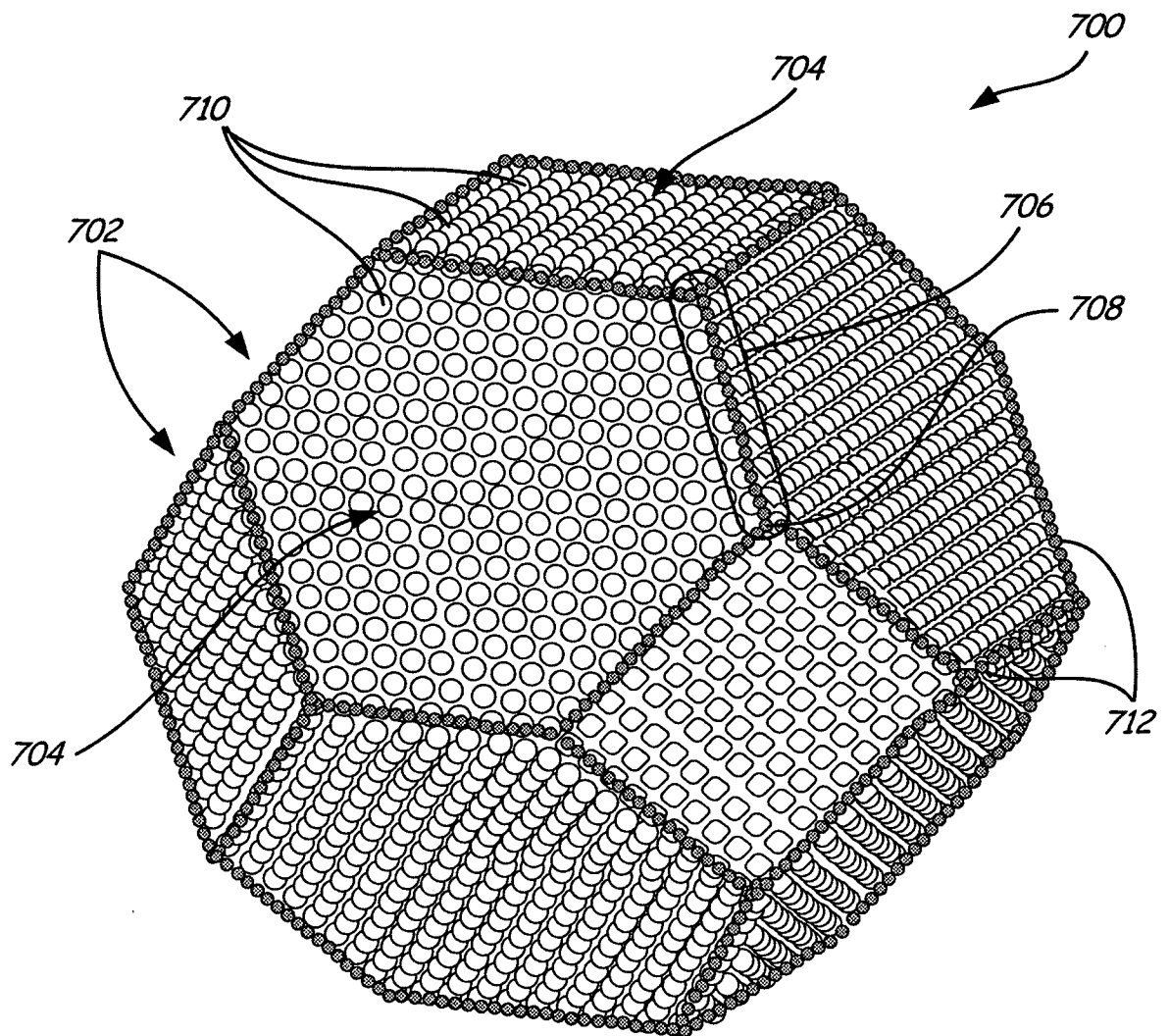
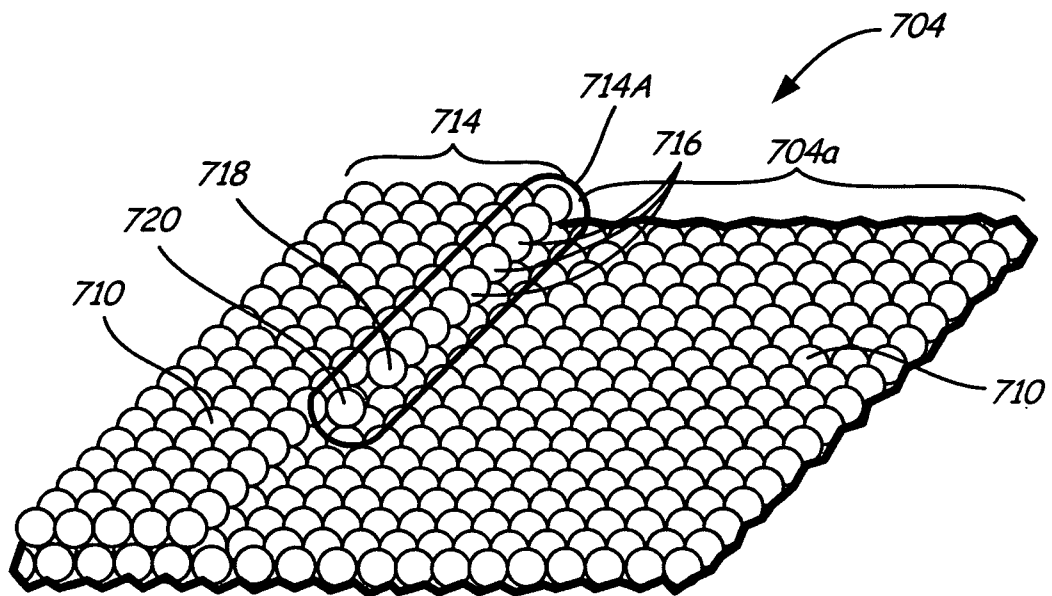
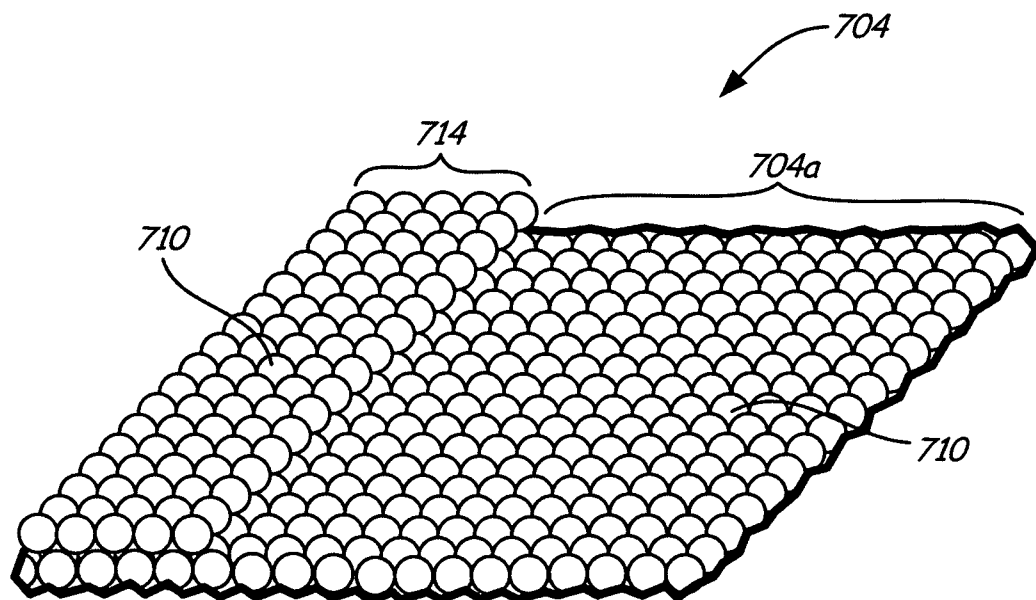
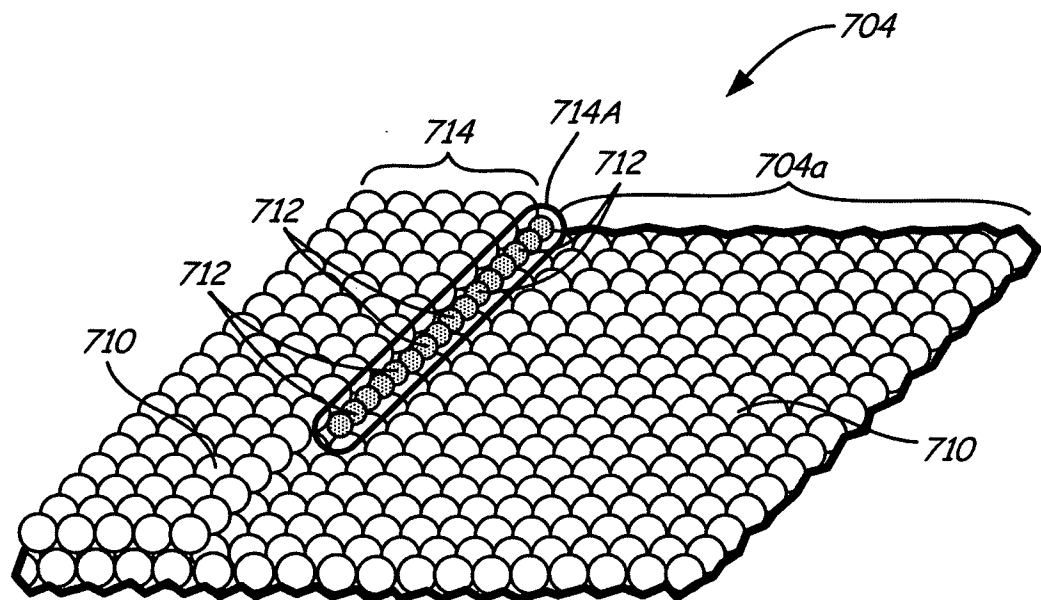
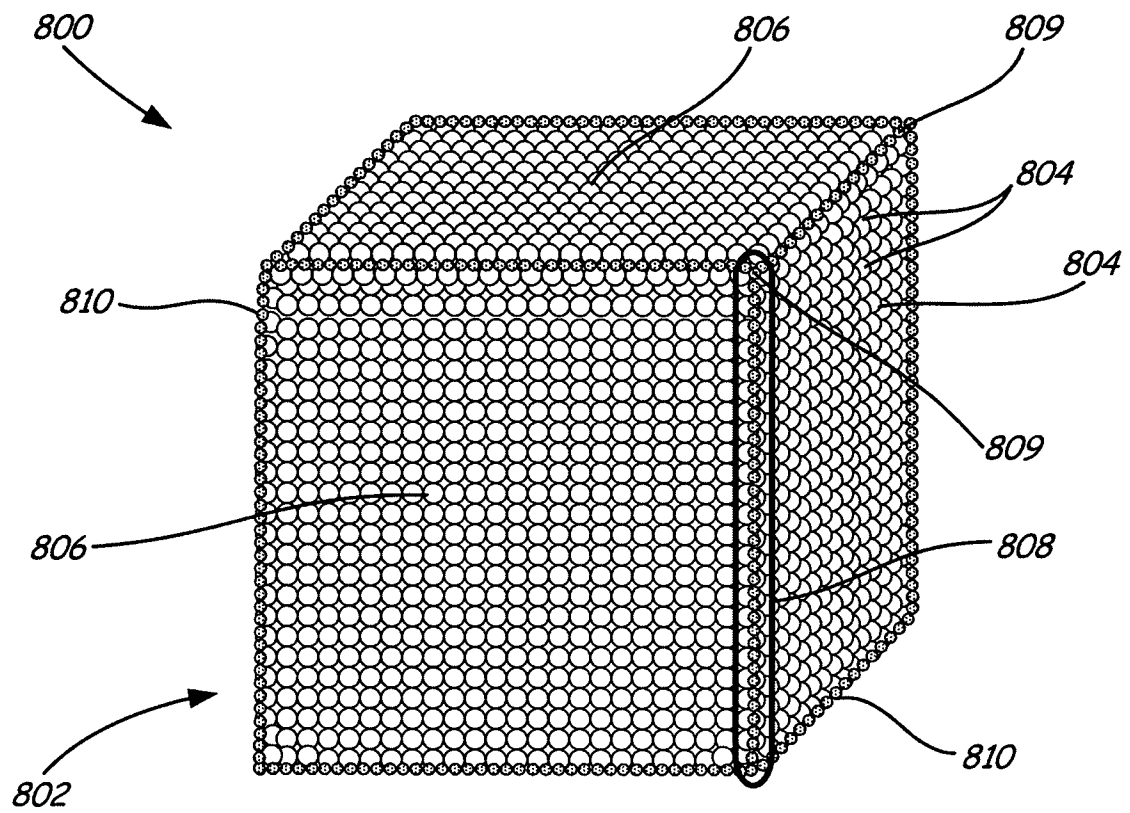


FIG. 11

12/16

*FIG. 12A**FIG. 12B*

*FIG. 12C*

*FIG. 13*

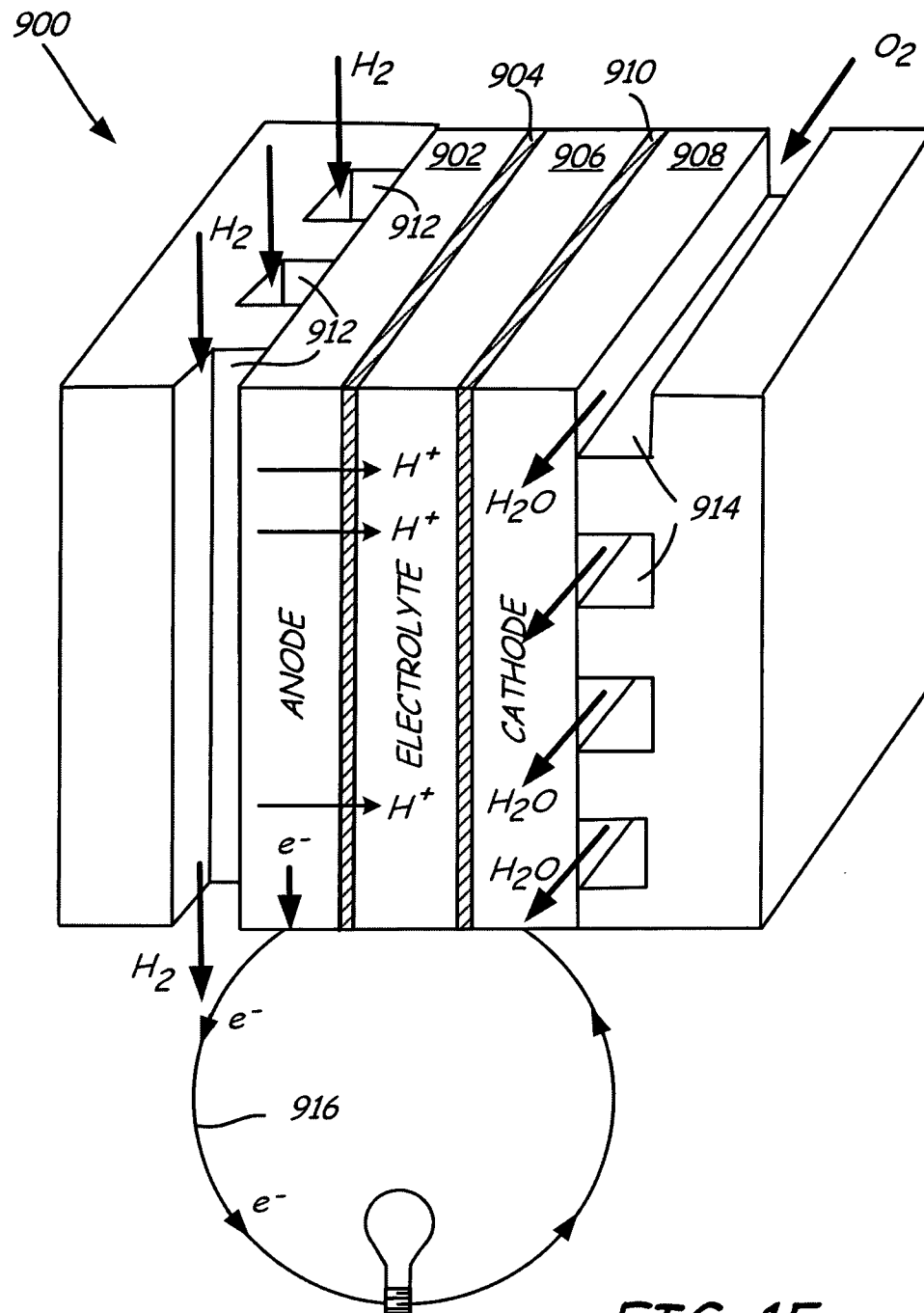


FIG. 15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2008/013333**A. CLASSIFICATION OF SUBJECT MATTER****B82B 3/00(2006.01)i, B82B 1/00(2006.01)i**

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)

IPC B01J, H01M

Documentation 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 since 1975

Japanese Utility models and applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKIPASS (KIPO internal) & Keywords: nano, Pt, catalyst, transition, metal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 7,125,822 B2 (NAKANO, YOSHIHIKO et al.) 24 October 2006 See claims 1-19	1-36
A	US 2007/0026294 A1 (SHIMAZAKI, YUZURU et al.) 01 February 2007 See claims 1-15	1-36
A	US 2004/0121219 A1 (MEI, WU et al.) 24 June 2004 See claims 1-19	1-36
A	US 2004/0087441 A1 (BOCK, CHRISTINA et al.) 06 May 2004 See claims 1-20	1-36



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 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

30 JUNE 2009 (30.06.2009)

Date of mailing of the international search report

30 JUNE 2009 (30.06.2009)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
Government Complex-Daejeon, 139 Seonsa-ro, Seo-
gu, Daejeon 302-701, Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

Park, Jong Chul

Telephone No. 82-42-481-8306



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2008/013333

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 7125822 B2	24.10.2006	US 2004-0072061 A1	15.04.2004
US 2007-0026294 A1	01.02.2007	NONE	
US 2004-0121219 A1	24.06.2004	JP 2004-079438 A JP 3651799 B2	11.03.2004 25.05.2005
US 2004-0087441 A1	06.05.2004	NONE	