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Cyclic Regeneration of Nanostructured Composites for Catalytic Applications

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(54) **CYCLIC REGENERATION OF NANOSTRUCTURED COMPOSITES FOR CATALYTIC APPLICATIONS**

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(71) Applicant: **The Curators of the University of Missouri, Columbia, MO (US)**

(57) **ABSTRACT**

(72) Inventor: **Fatih Dogan, Rolla, MO (US)**

A cermet catalyst material, defining a matrix having interconnected open pores, the matrix selected from the group consisting of YSZ and CGO and defining a substrate, a ceramic coating having a general formula $A_yB_nO_x$ at least partially coating the pores, and a plurality of metal particles A at least partially embedded in the ceramic coating. A is selected from the group consisting of Co, Cu, Ce, Ni, Ti, and combinations thereof and B is selected from the group consisting of Mo, W, Ce, and combinations thereof. When the coating is in a first oxidizing atmosphere and at a temperature between 400 degrees Celsius and 800 degrees Celsius the metal particles are absorbed into the coating in the form of metal cations, giving the coating the general formulation $A_yB_nO_x$. When the coating is in a reducing atmosphere and at a temperature between about 400 degrees Celsius and about 800 degrees Celsius the B metal cations emerge from the coating to yield a plurality of B metal particles at least partially embedded in the coating, wherein the reduced coating has a general formula $A_{y-z}B_nO_x$, wherein $y > z$ and $x' > x$.

(21) Appl. No.: **16/677,779**

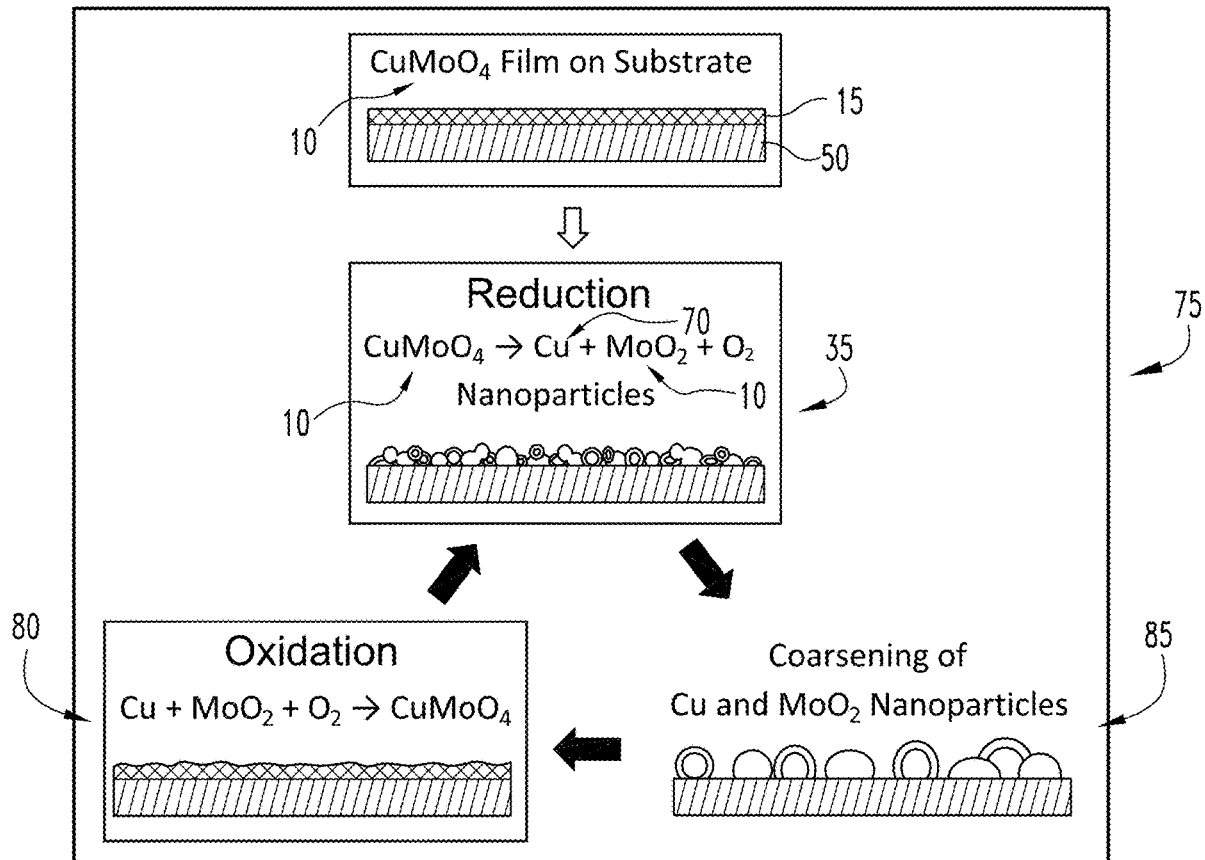
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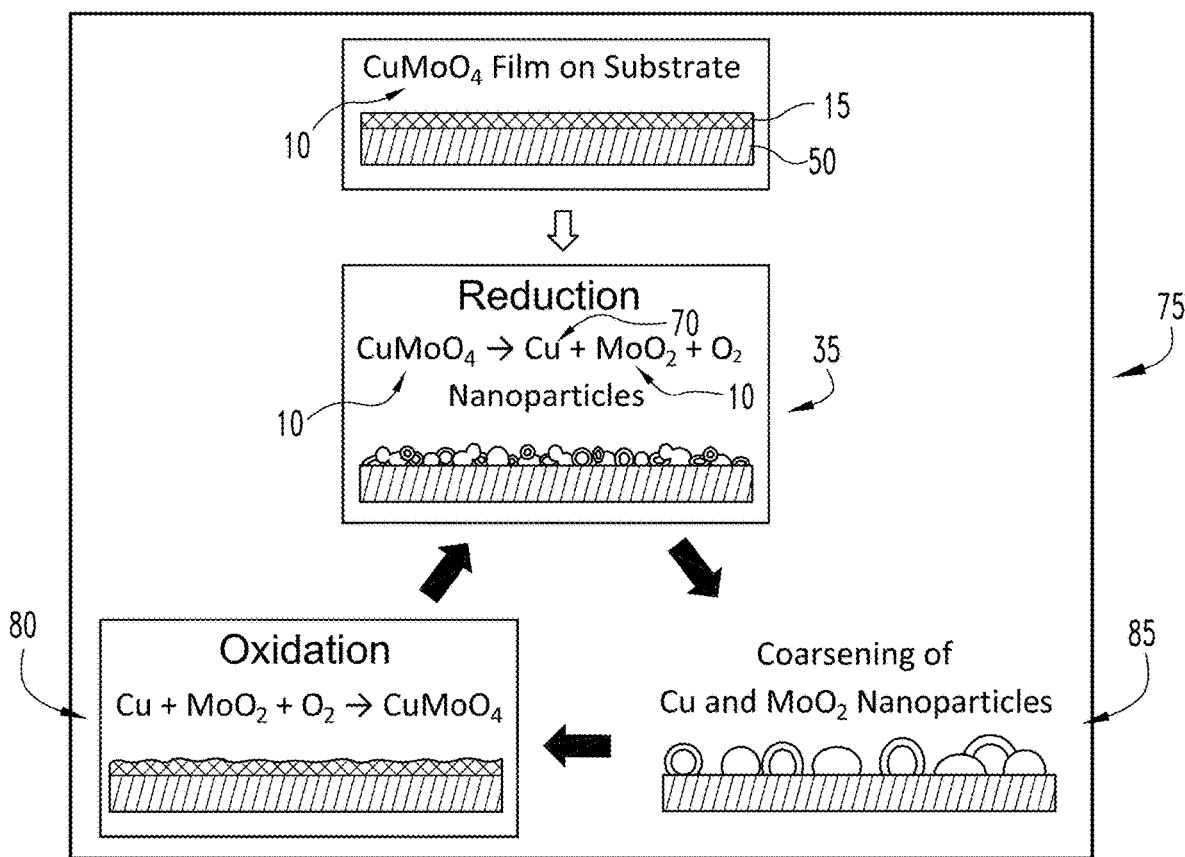


Fig. 1

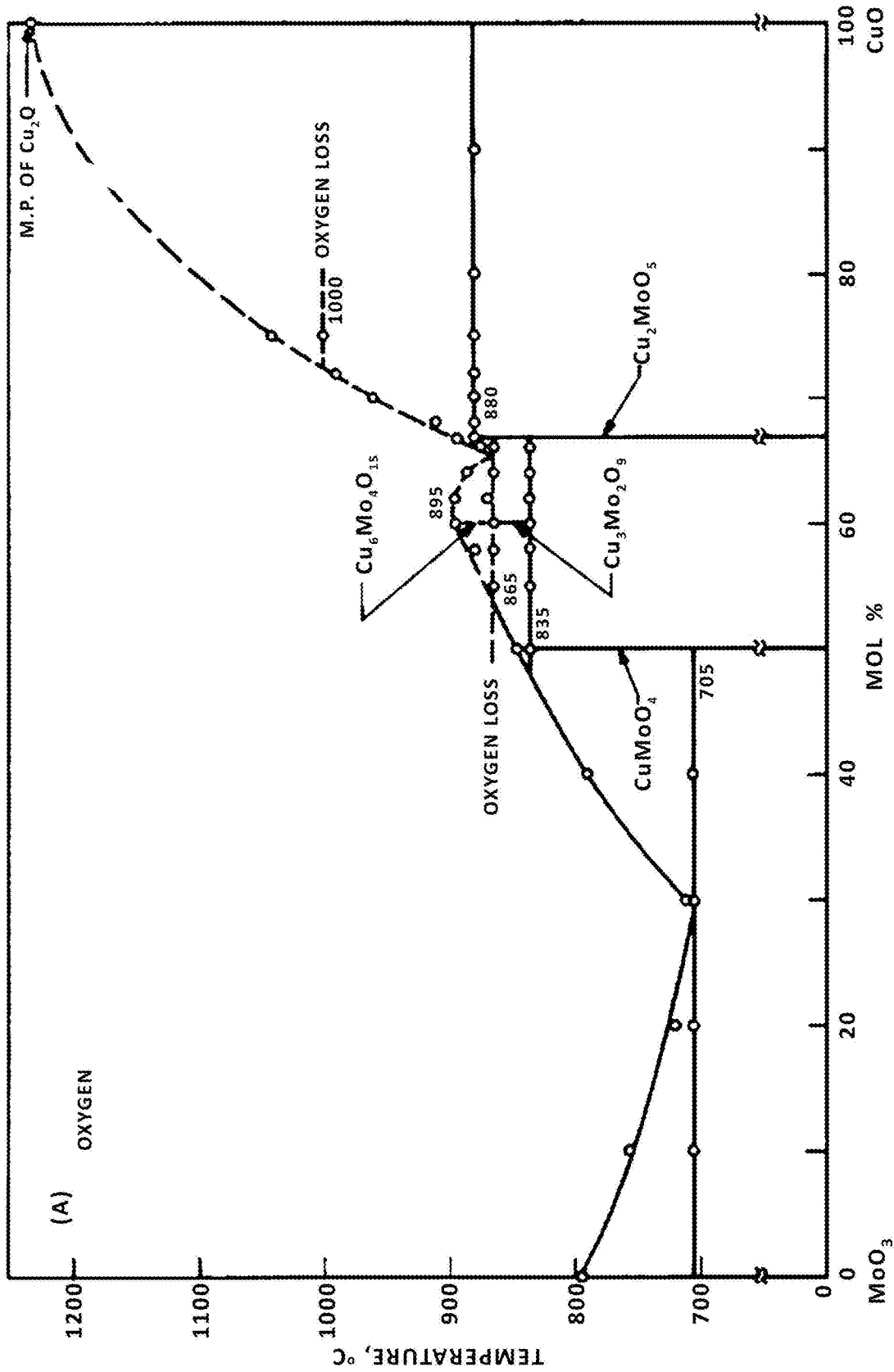


Fig. 2A

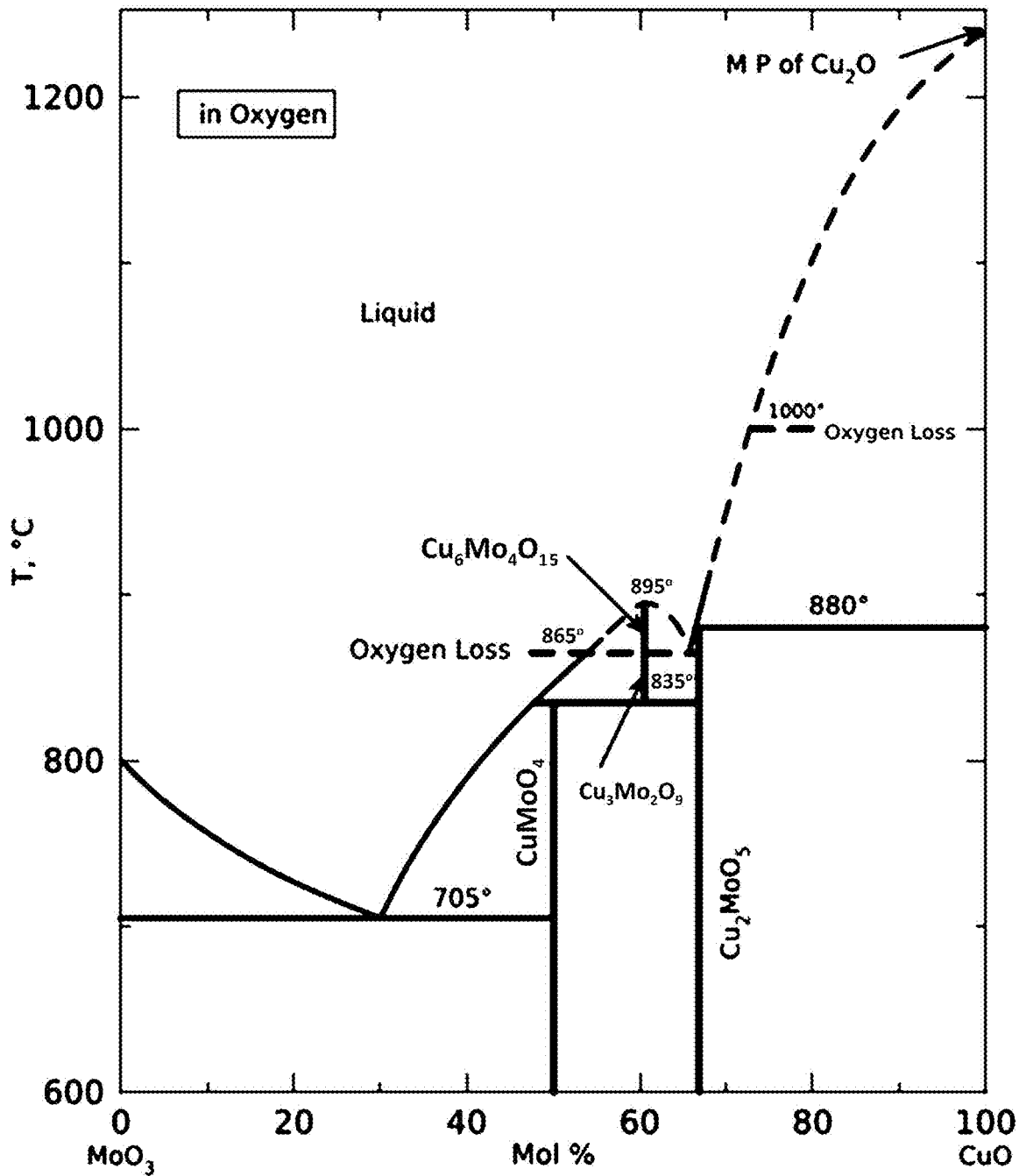


Fig. 2B

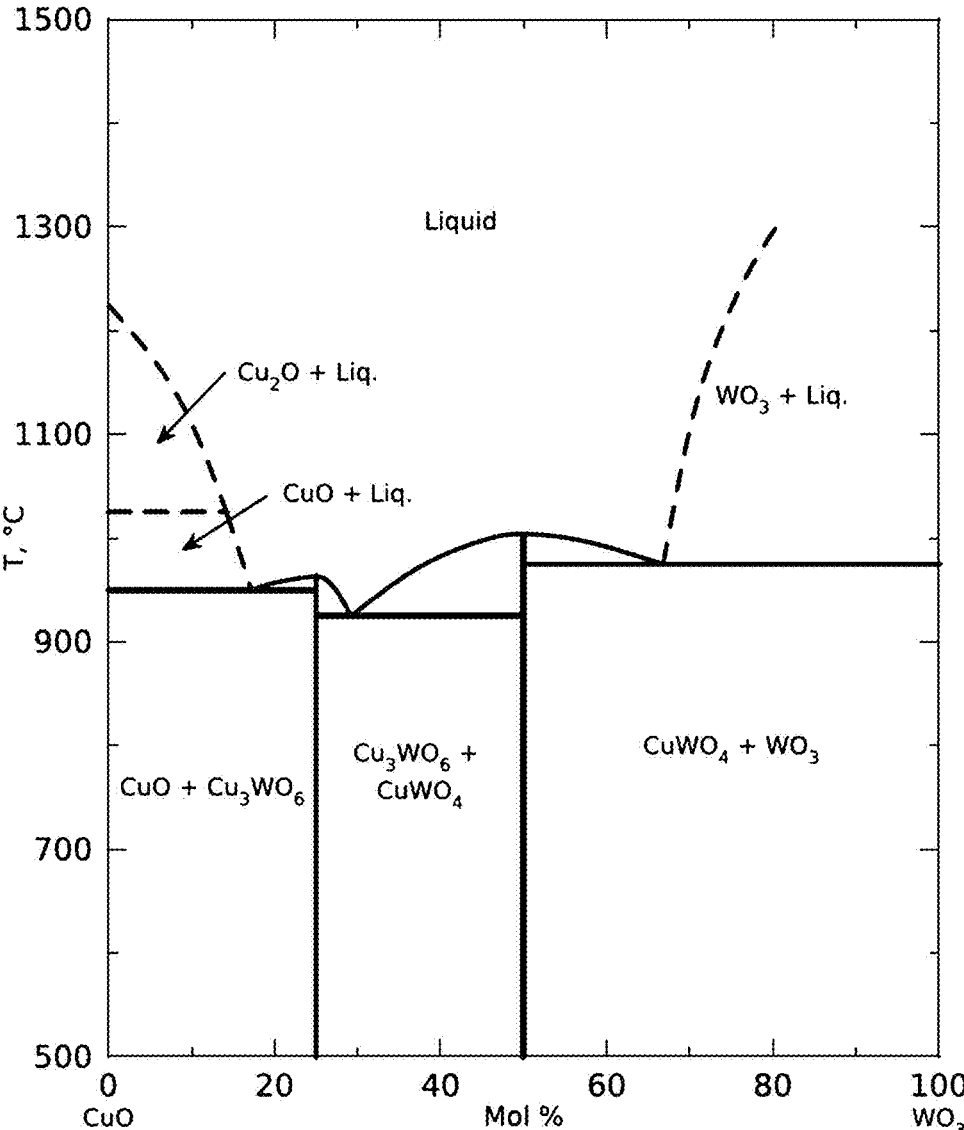


Fig. 2C

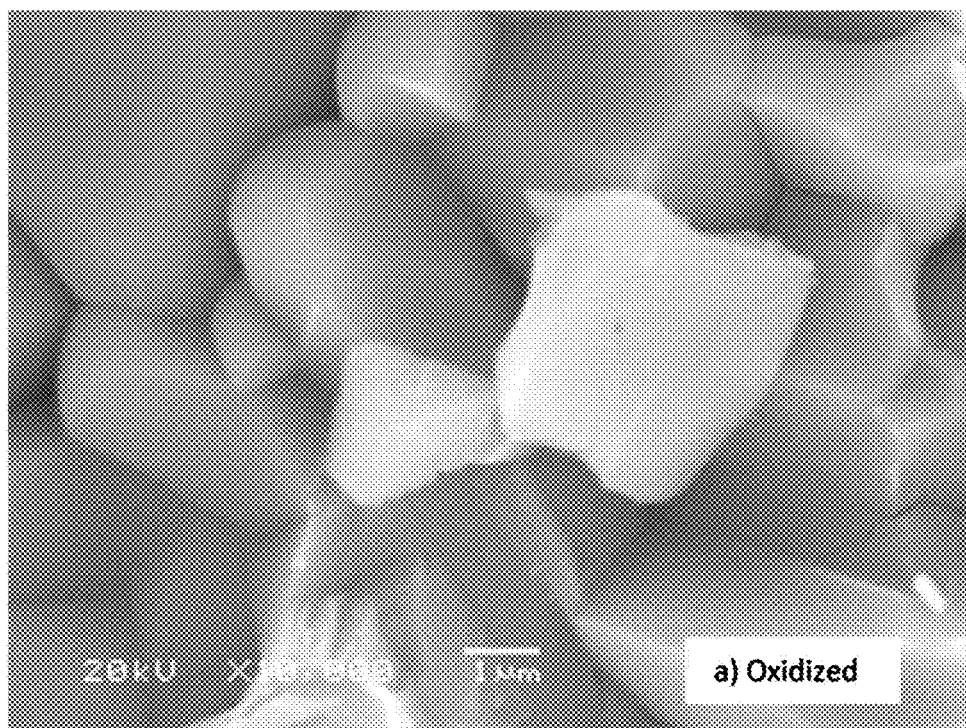


Fig. 3A

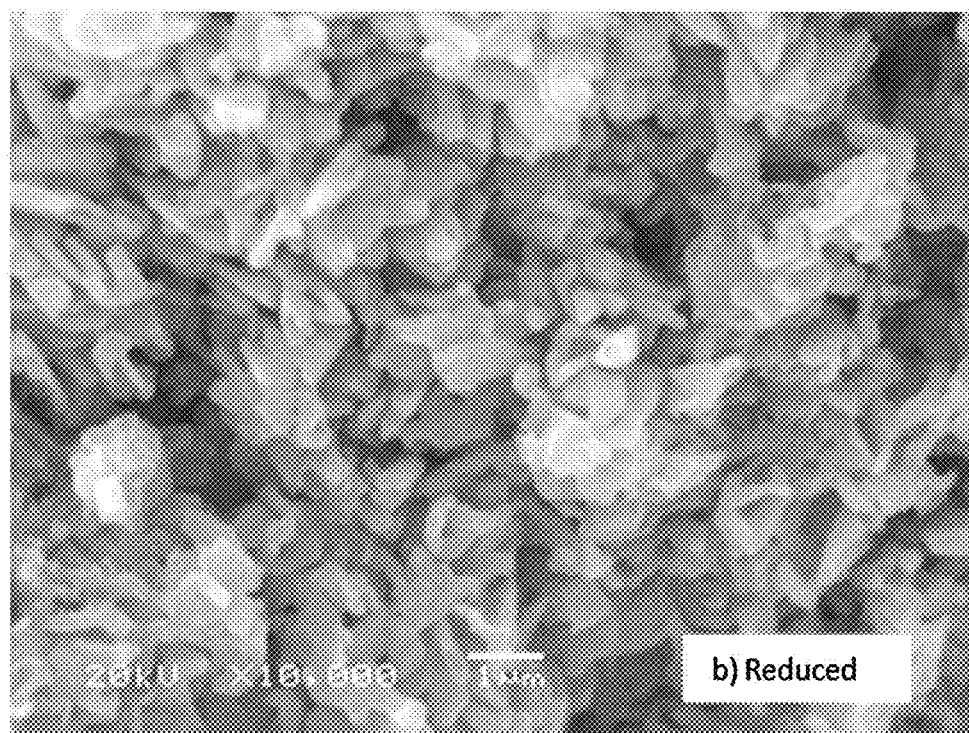


Fig. 3B

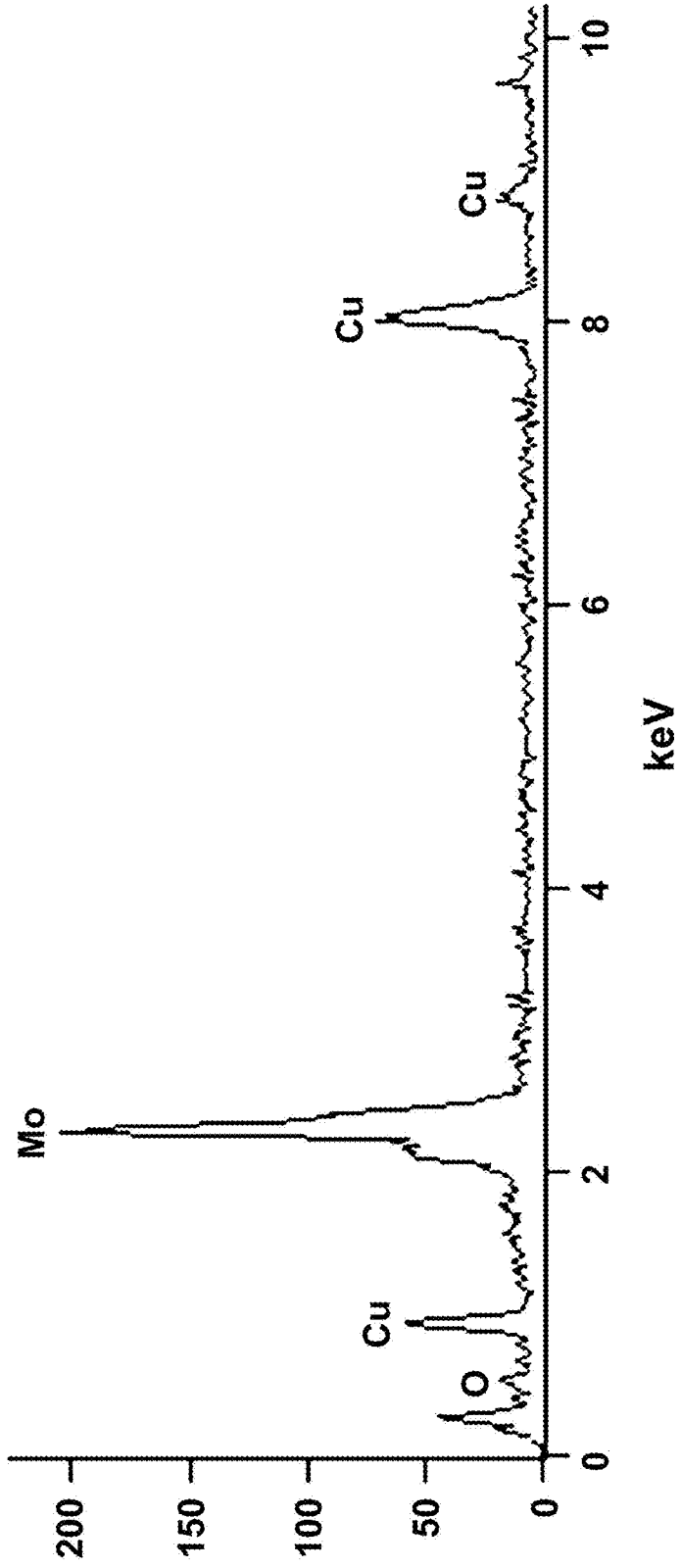


Fig. 3C

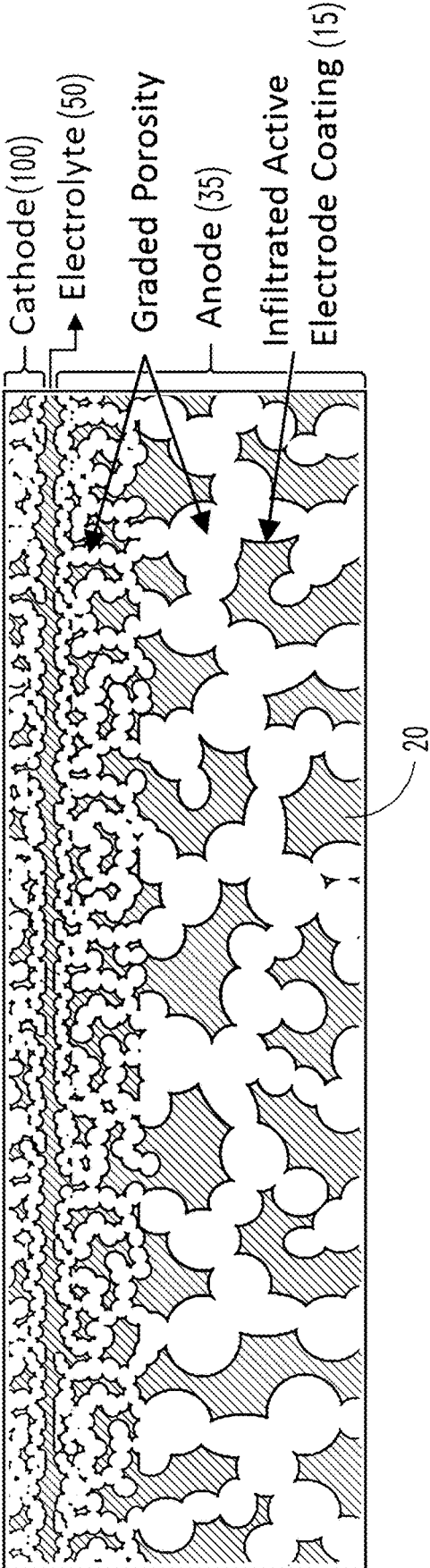


Fig. 4

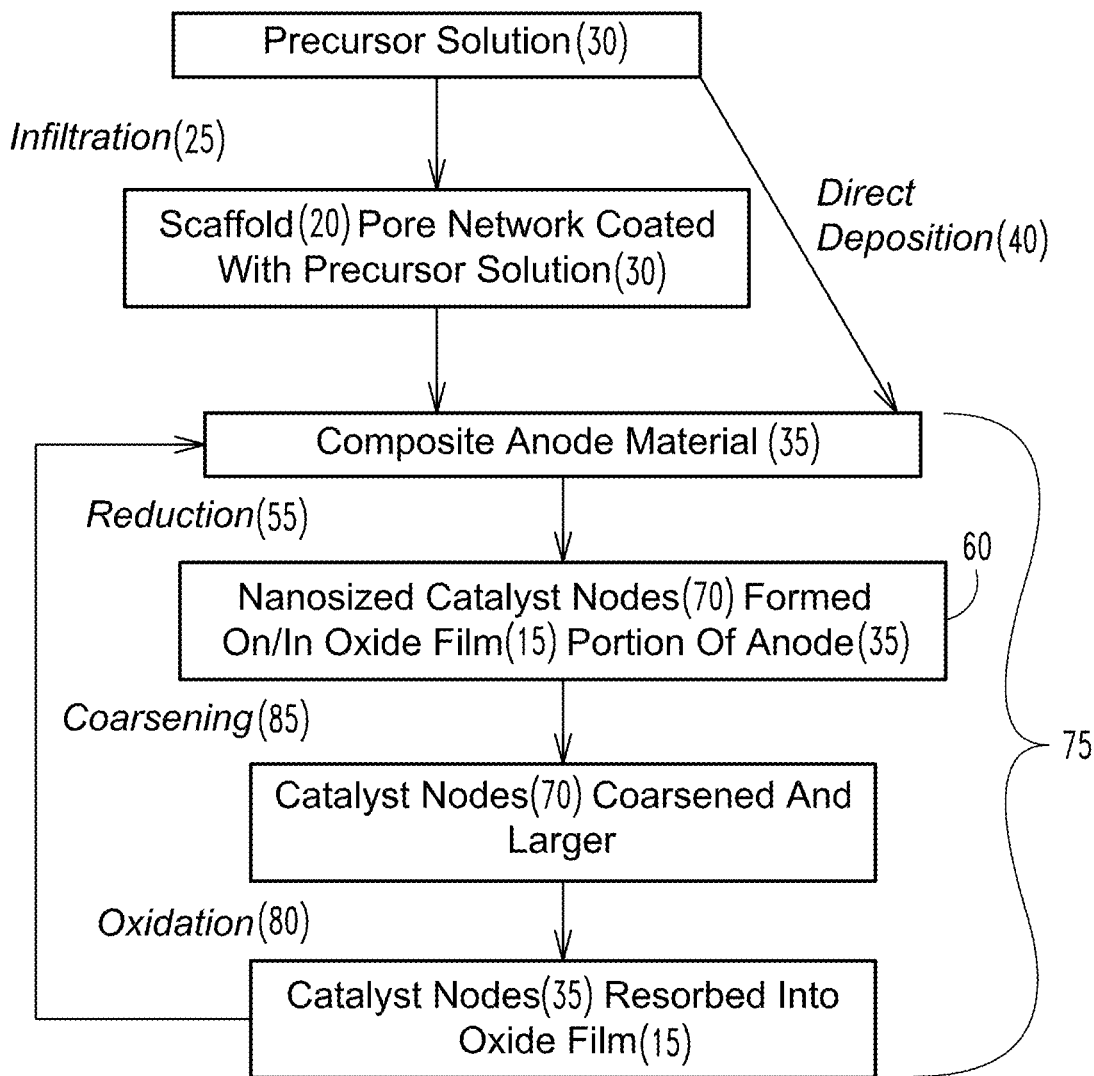


Fig. 5

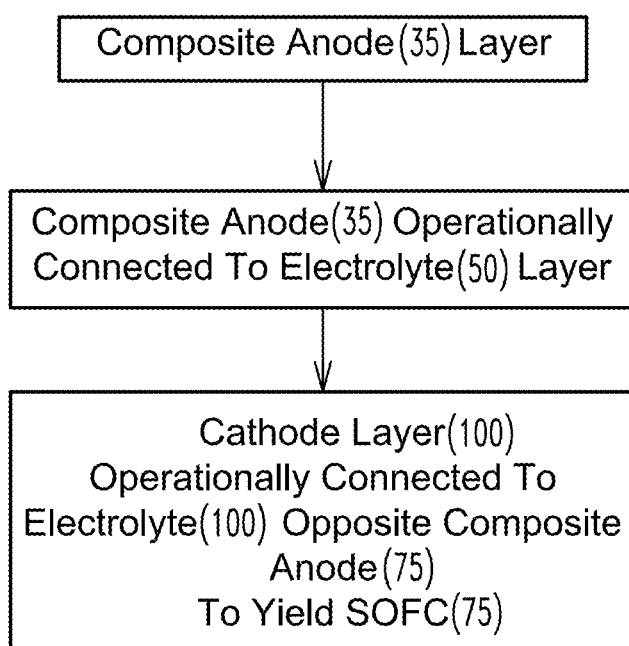


Fig. 6

CYCLIC REGENERATION OF NANOSTRUCTURED COMPOSITES FOR CATALYTIC APPLICATIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This patent application claims priority to co-pending U.S. patent application Ser. No. 15/488,668, filed on Apr. 17, 2017, which claimed priority to then co-pending provisional patent application Ser. No. 62/325,206, filed on Apr. 20, 2016.

BACKGROUND

[0002] Nanosized particles of high surface area are useful in many catalytic applications. However, the progressive coarsening of such nanosized particles in environments of elevated temperatures tends to have an adverse effect on their catalytic performance. Long-term stability of solid oxide fuel cells (SOFC) and other high temperature electrochemical cells would be significantly improved by repetitive regeneration of nanostructured catalysts to mitigate the deleterious effects of particle growth under operating conditions. Thus, there remains a need for nanostructured catalysts that may survive repeated duty cycles and/or exhibit regenerative behavior. The present novel technology addresses this need.

BRIEF DESCRIPTION OF THE DRAWINGS

[0003] FIG. 1 schematically illustrates the coarsening and regeneration cycle for metal oxide catalysts.

[0004] FIG. 2A is a phase diagram of the MoO_3 —CuO system.

[0005] FIG. 2B is a phase diagram of the MoO_3 —CuO system.

[0006] FIG. 2C is a phase diagram of the WO_3 —CuO system.

[0007] FIG. 3A is a photomicrograph of CuMoO_4 after sintering in air at 800°C .

[0008] FIG. 3B is a photomicrograph of CuMoO_4 after reduction at 400°C .

[0009] FIG. 3C is a schematic illustration of the EDS spectra for the sample of FIG. 3B.

[0010] FIG. 4 is a schematic illustration of graded porosity of the electrodes for anode supported cell with a thin electrolyte layer, with anode and cathode infiltrated with catalytic precursor solutions under vacuum followed by heat treatment.

[0011] FIG. 5 is a flow chart schematically illustrating the preparation and operation of a cyclically regenerable composite oxide anode material.

[0012] FIG. 6 is a flow chart schematically illustrating a solid oxide fuel cell (SOFC) incorporating a composite oxide anode material.

DETAILED DESCRIPTION

[0013] For the purposes of promoting an understanding of the principles of the novel technology, reference will now be made to the embodiments illustrated in the drawings and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the novel technology is thereby intended, such alterations and further modifications in the illustrated device, and such further applications of the principles of the novel technology

as illustrated therein being contemplated as would normally occur to one skilled in the art to which the novel technology relates.

[0014] As illustrated in FIGS. 1-6, the novel technology relates to solid solutions of specific oxides **10** (such as CuMoO_4 and CuWO_4 solid solutions) that can be phase separated in reducing atmospheres to form nanosized particles **70** (such as Cu catalyst dispersed in MoO_2 , Cu catalyst dispersed in WO_2) as well as methods for the implementation of the same. The novel technology specifically relates to (i) the deposition of oxide films **15** (such as CuMoO_4 and CuWO_4) into porous scaffolds **20** of yttria-stabilized zirconia (YSZ) by infiltration **25** of polymeric precursor solutions **30** to yield composite anodes **35**, (ii) the direct deposition **40** of composite (such as CuMoO_4 —YSZ and CuWO_4 —YSZ) films **35** on dense YSZ electrolytes **50**, (iii) the reduction **55** of oxides **10** to form redox stable nanostructured anodes **60** (such as Cu— MoO_2 and Cu— WO_2) having distributed nanoscale catalyst nodes **70** for operation of SOFC using hydrogen and hydrocarbon fuels, respectively, (iv) the redox process for cyclic regeneration **75** of nanostructured catalysts **70** by utilizing of surface/microstructural characterization techniques and theoretical modeling; and (v) improvement of the electrochemical performance of nanostructured SOFC anodes **35** as regenerated under cyclic redox conditions.

[0015] This cyclical regeneration **75** of catalyst material **70** exploits (i) reversible formation of nanostructured cermets from multicomponent oxides **15** that form solid solutions; and (ii) redox stability of solid oxide fuel cells (SOFC) **90** that can be reconditioned by restoring the catalytic activity of the anodes **35**. Although SOFCs **90** have several advantages including fuel flexibility, high efficiency, co-generation of heat and power, their widespread use has not yet been realized primarily due to temperature-dependent materials issues. To address the high temperature instability of traditional anode materials, nanostructured composite coatings **35** are deposited by: (i) infiltration **25** of precursor solutions **30** into the porous scaffolding **20** of anode supported YSZ electrolyte **55**; and (ii) direct deposition **40** of the precursor solutions (CuMoO_4 —YSZ or CuWO_4 —YSZ) using pore formers on the YSZ electrolyte **55**. In the latter case, YSZ particles form a porous scaffold **20** surrounded by the CuMoO_4 or CuWO_4 phase during sintering in air. Under reducing atmosphere, CuMoO_4 and CuWO_4 decompose to Cu— MoO_2 and Cu— WO_2 cermets inside of the YSZ scaffold supporting the YSZ electrolyte. Percolation of the individual phases may be controlled by changing the stoichiometric ratio of the cations, and is a function of the size of the particles after the reduction process occurs, as coarsening of particles may lead to a loss of percolation. The interaction of the oxide particles with copper particles may be exploited to hinder sintering and coarsening **85** of the nanosized percolated copper particles at elevated temperatures, such as by Ostwald Ripening. Stability of the cermets (resistance to sintering) arising from the strength of interatomic bonds at the interface of the metal and oxide particles, such as in Cu— MoO_2 and Cu— WO_2 cermet systems, are exploited on YSZ scaffold or dense electrolyte. Further, variations of metal **70** and metal oxide **10** interfaces may be done to enhance their catalytic activity for oxidation of hydrogen and hydrocarbon fuels in solid oxide fuel cells, as the interfacial area between the nanoscale metal **70** and metal oxide **10** particles is much greater as there are more

catalytically active sites as compared to coarsened particles. The size of metallic particles **70** are in the range of 1-500 nm during the initial operation conditions of the anode **35** after reduction. Their size become 0.5-3 micrometer when coarsened.

[0016] Sintering of nanoparticles **70** in SOFC anodes **60** that leads to deactivation of the catalyst may be reversed by oxidation/reduction redispersion process. A novel Cu—MoO₂ composite anode material **15** is utilized to form CuMoO₄ upon oxidation **80** and phase separates under a reducing atmosphere. Such anode structures **15**, supported on porous solid electrolytes **50**, may also be redox stable to prevent cracking or spallation of anodes during the cyclic oxidation/reduction process.

[0017] The following reactions are examples of what occurs during the redox process using H₂ and O₂ reducing and oxidizing gas atmospheres, respectively. Instead of hydrogen fuel, various hydrocarbon fuels C_xH_y, or CO gas can be utilized to control the reduction reaction.

[0018] Reduction: $\text{CuMoO}_4 + 2\text{H}_2 \rightarrow \text{Cu} + \text{MoO}_2 + 2\text{H}_2\text{O}$
400° C.

[0019] Oxidation: $\text{Cu} + \text{MoO}_2 + \text{O}_2 \rightarrow \text{CuO} + \text{MoO}_3 \rightarrow \text{CuMoO}_4$ 600° C.

[0020] Depending on the Cu/Mo ratio of the compositions, other phases such as Cu₂MoO₅ and their combination with CuO may form according to the binary phase diagram. In oxygen, CuMoO₄ melts incongruently at 835° C., and at atmospheric pressure Cu₃Mo₂O₉ exists only between this temperature and 865° C., where it transforms to cuprous Cu₆Mo₄O₁₅, which melts congruently at 895° C. Cu₂MoO₅ melts peritectically at 880° C. The MoO₃—CuMoO₄ eutectic occurs near 30 mol % CuO at 705° C.

[0021] Traditional single-phase MoO₂ anode single cells have been operated at 750° C. for relatively short time frames. There are two reasons that this operating temperature is too high for a practical hydrocarbon fueled SOFC stack. First, though it is possible to test button cells without metallic balance of plant hardware in the fuel flow path, practical systems will utilize metal tubing and metal interconnects which will template carbon deposition at lower temperatures than those used in single cell tests. Secondly, molybdenum oxides have a very high vapor pressure at 750° C. and above, and may rapidly evaporate into the flowing anode exhaust stream over time or during the envisioned redox regeneration cycles. Lower temperature SOFC operation has been demonstrated using anode **35** supported thin film electrolyte **50** designs based on conventional SOFC material sets such as Ni—YSZ cermet anode **35**, YSZ electrolyte **50**, and LSM cathode **100**. While molybdenum oxides have high vapor pressure at 750° C. and above, MoO₂ can be replaced with WO₂ (melting temperature: 1700° C.) for operation of SOFC at higher temperatures.

[0022] For the redispersion of sintered Cu and MoO₂ nanoparticles in anodes of SOFC, typical materials combinations exhibit (i) optimum Mo/Cu ratio to utilize the catalytic activity of MoO₂ efficiently as Cu by itself is a weak catalyst for oxidation hydrocarbon fuels, (ii) transport phenomena and kinetics during phase transformations as a function of temperature, (iii) percolation of Cu and MoO₂ depending on the molar ratio of both phases, (iv) effect of surface curvature of support material (flat vs porous) on the redox stability of the films, (v) nucleation/growth and dissolution of individual phases depending on temperature and

time, and (vi) Cu/MoO₂ interface reactions and contribution of the interface to catalytic activity of the anode.

[0023] Of particular advantage are molybdenum oxides (such as MoO₂ and MoO₃) that can form solid solutions of multicomponent compounds with other metal oxides, typically in the form of thin films or coatings, and are compatible with the substrate materials (e.g. YSZ, doped ceria for SOFC) at elevated temperatures (specifically, they do not form undesired phases that may impede performance of high temperature electrochemical devices). Electrode materials should also be electrically conducting while they are catalytically active. Percolation of the conducting phase (for example, MoO₂ has high mixed electronic and ionic conductivity) is appreciated, while the phase of lower conductivity may be catalytically active. Some typical compounds include MoO₂—CuO; MoO₂—CeO; MoO₂—CoO; MoO₂—TiO₂; MoO₂—NiO; MoO₂—Y₂O₃; MoO₂—WO₂; MoO₂—CeO₂—ZrO₂; MoO₂—CuO—CeO₂—ZrO₂; CuO—CeO₂; NiO—Al₂O₃; NiO—Al₂O₃—ZrO₂; NiO—La₂O₃; NiO—WO₃ and CuO—WO₃.

Example 1

[0024] Electrolyte supported cells are prepared using yttria-stabilized zirconia (YSZ, 8 mol % Y₂O₃) substrates (thickness 100-200 μm) as a dense solid electrolyte, lanthanum strontium manganese (LSM) or lanthanum strontium cobalt ferrite (LSCF) as a cathode, and copper molybdate CuO—MoO_x (x=0.5-3) as an anode. The Cu/Mo ratio of the oxide may vary within the solid solubility of both oxide components.

[0025] A porous YSZ tape (10-100 μm thick) is sintered on the anode site of the dense YSZ electrolyte that serves as a scaffold for infiltration of Cu—Mo—O precursor solutions. Porosity and pore size distribution of YSZ scaffolds are controlled with fugitive pore formers decomposing upon heating. Copper molybdate compositions with optimum Cu/Mo ratios are synthesized as polymeric precursor solutions using soluble copper and molybdenum salts with ethylene glycol for polymerization and butoxy ethanol as wetting agent. The concentrated solutions of optimized viscosity are deposited onto porous YSZ scaffold through vacuum infiltration into the pores and heat treatment processes. The thickness of the Cu—Mo—O coatings can vary typically between 10-1000 nanometers.

[0026] Precursor solution of LSM, LSCF, or other perovskites are deposited on the cathode site by applying of the same method as described for the anode or simply by screen printing of the cathode inks on the dense electrolyte.

[0027] The resultant cells are tested between 400° C. and 800° C. using hydrocarbon fuels (such as methane, propane or vaporized gasoline). The fuels are mixed with CO₂ and air to stabilize the MoO₂ phase (to avoid eutectic melting) during the reduction of Cu—Mo—O solid solution. The reduction process leads to formation of nanostructured Cu and MoO₂ particles (phases) of high catalytic activity required for oxidation of fuel efficiently and for achieving of high power densities of the cell. However, nanostructured particles tend to coarsen with time at operating temperatures and become catalytically less active, which, in turn, results in lowering of the power density of the cell.

[0028] Nanosized Cu and MoO₂ particles are regenerated by exposing the anode to an oxidizing atmosphere (such as air or flowing oxygen) so that both solid phases react, diffuse into each other and return to a Cu—Mo—O solid solution.

After switching of air to fuel gas, Cu—Mo—O phase is reduced by regenerating of catalytically active nanosized Cu and MoO₂ particles. The anode coating within the YSZ scaffold is redox stable under repetitive cycling conditions of the cell to operate the fuel cell extended period of time with high efficiency using hydrocarbon fuels.

Example 2

[0029] The same procedure described in Example 1 can be implemented using doped ceria (such as CGO, Gd-doped CeO₂) electrolytes instead of YSZ to operate the cells at lower temperatures.

Example 3

[0030] The Cu—Mo—O anode system above is replaced with a Cu—Ce—O system that can also form solid solutions at lower concentrations of CuO in CeO₂ (typically, about <20% CuO). The same procedures described under Examples 1 and 2 are applied for Cu—CeO₂ catalysts.

Example 4

[0031] The Cu—Mo—O system above is replaced with a Cu—W—O system that has relatively higher eutectic melting temperatures and lower vapor pressure but similar catalytic and electrical properties.

Example 5

[0032] An anode supported cell with a dense and thin layer of YSZ (or CGO) electrolyte (<10 μm) on a porous YSZ or CGO scaffold (thickness about 0.5 to 1 mm) as anode support is prepared. The cells are processed and operated as described in Examples 1-4.

General Examples

Metal Oxides: AO, BO, CO (Mixed in Various Ratios)

[0033] The following reactions depend on the oxygen partial pressure. Under strong reducing conditions (such as in H₂) oxide compounds can be reduced completely to metal. In case of hydrocarbon fuels, oxygen partial pressure can be relatively high so that thermodynamically less stable oxides are reduced while more stable metal oxides are partially reduced and can be oxygen deficient.

[0034] AO+BO: ABO→A+BO→ABO

[0035] CuO+MoO₂: CuMoO₄ (or Cu₂MoO₆)→Cu+MoO₂→CuMoO₄ (or Cu₂MoO₆)

[0036] NiO+MoO₂: NiMoO₄→Ni+MoO₂→NiMoO₄

[0037] CuO+WO₂: CuWO₄ (or Cu₃WO₆)→Cu+WO₂→CuWO₄ (or Cu₃WO₆)

[0038] NiO+WO₂: NiWO₄→Ni+WO₂→NiWO₄

[0039] AO+BO+CO: ABCO→A+BCO→ABCO

[0040] CuO+MoO₂+WO₂: CuMoWO_x→Cu+(Mo, W)O₂ ss→CuMoWO_x

[0041] NiO+MoO₂+WO₂: NiMoWO_x→Ni+(Mo, W)O₂ ss→NiMoWO_x

[0042] AO+BO: ABO (solid solution (ss))→A+BO (reduction)→ABO ss (reoxidation)

[0043] MoO₂+TiO₂: (Mo, Ti)O₂ ss→Mo+TiO₂ (reduction)→(Mo, Ti)O₂ ss (reoxidation)

Reaction temperatures are typically between 200 degrees Celsius and 1000 degrees Celsius, more typically between 400 degrees Celsius and 800 degrees Celsius.

[0044] In general, the ceramic coating has a general formula A_yB_nO_x, with n, y and x having values that fulfill the stoichiometric obligations arising from the specific metal cations selected for A and B, and A and B are different. Typically, A is selected from the group consisting of Co, Cu, Ni, Ti, and combinations thereof and B is selected from the group consisting of Mo, W, Ce, and combinations thereof. More typically, A is selected from the group consisting of Cu, Ni, and Co, and B is selected from the group consisting of Mo and W. Still more typically, A is selected from the group consisting of Cu and Ni. When the coating is in a first oxidizing atmosphere (having a first oxygen partial pressure) and at a temperature between 400 degrees Celsius and 800 degrees Celsius, the A metal particles are absorbed into the coating in the form of metal cations, giving the coating the general formulation A_yB_nO_x. When the coating is in a reducing atmosphere (having a second oxygen partial pressure less than the first oxygen partial pressure) and at a temperature between about 400 degrees Celsius and about 800 degrees Celsius the A metal cations emerge from the coating to yield a plurality of A metal particles at least partially embedded in the coating, wherein the reduced coating has a general formula A_{y-z}B_nO_x, wherein y>z and wherein x'[>]x.

[0045] While the novel technology has been illustrated and described in detail in the drawings and foregoing description, the same is to be considered as illustrative and not restrictive in character. It is understood that the embodiments have been shown and described in the foregoing specification in satisfaction of the best mode and enablement requirements. It is understood that one of ordinary skill in the art could readily make a high-infinite number of insubstantial changes and modifications to the above-described embodiments and that it would be impractical to attempt to describe all such embodiment variations in the present specification. Accordingly, it is understood that all changes and modifications that come within the spirit of the novel technology are desired to be protected.

I claim:

1. A cermet catalyst material, comprising:

a matrix having interconnected open pores, the matrix selected from the group consisting of YSZ and CGO and defining a substrate;

a ceramic coating having a general formula A_yB_nO_x at least partially coating the pores; and

a plurality of metal particles A at least partially embedded in the ceramic coating;

wherein A is selected from the group consisting of Co, Cu, Ce, Ni, Ti, and combinations thereof;

wherein B is selected from the group consisting of Mo, W, Ce, and combinations thereof;

wherein when the at coating is in a first oxidizing atmosphere and at a temperature between 400 degrees Celsius and 800 degrees Celsius the metal particles are absorbed into the coating in the form of metal cations, giving the coating the general formulation A_yB_nO_x; and

wherein when the coating is in a reducing atmosphere and at a temperature between about 400 degrees Celsius and about 800 degrees Celsius the B metal cations emerge from the coating to yield a plurality of B metal particles at least partially embedded in the coating, wherein the reduced coating has a general formula A_{y-z}B_nO_x;

wherein y>z; and wherein x'[>]x.

2. The cermet catalyst material of claim 1 wherein the A metal particles are between 1 nanometer and 100 nanometers across and wherein the A metal particles are generally positioned at grain boundaries, grain surfaces and in intragranular pores.

3. A method for preparing a catalytic cermet material, comprising:

infiltrating an interconnected open pore network extending throughout a substrate member with a solution of A and B cations to yield an infiltrated substrate, wherein the substrate is selected from the group consisting of YSZ and CGO, wherein A is selected from the group consisting of Co, Cu, Ce, Ni, Ti, and combinations thereof; wherein B is selected from the group consisting of Mo, W, Ce, and combinations thereof, and wherein A and B are different;

heating the infiltrated substrate to yield a coated substrate with an ABO layer coating at least some of the pores; and

generally evenly dispersing metal particles throughout the pore network;

wherein the metal particles are positioned on and in the coating;

wherein the coating has a general formula $A_{y-z}B_nO_x$;

wherein reducible A metal cations may be absorbed into the coating at elevated temperatures in an oxidizing atmosphere, driving the value of z to approach zero.

4. The method of claim 3 wherein absorbed metal cations are desorbed from the coating upon exposure to elevated temperatures in a reducing atmosphere.

5. The method of claim 3 wherein the oxidizing atmosphere has a first oxygen partial pressure and wherein the reducing atmosphere has a second, lower oxygen partial pressure.

6. The method of claim 3 and further comprising: operationally connecting the coated substrate to an electrolyte layer; and connecting a cathode layer to the electrolyte layer to define a fuel cell.

7. A cermet catalyst material, comprising:

a matrix having interconnected open pores, the matrix selected from the group consisting of YSZ and CGO and defining a substrate;

a ceramic coating having a general formula $A_yB_nO_x$ at least partially coating the pores; and

a plurality of metal particles A at least partially embedded in the ceramic coating;

wherein A is selected from the group consisting of Co, Cu, Ce, Ni, Ti, and combinations thereof;

wherein B is selected from the group consisting of Mo, W, Ce, and combinations thereof;

wherein metal particles are absorbed into the coating in the form of metal cations, giving the coating the general formulation $A_yB_nO_x$; and

wherein when the coating is in a reducing atmosphere and at a temperature between 400 degrees Celsius and 800 degrees Celsius, B metal cations emerge from the coating to yield a plurality of B metal particles at least partially embedded in the coating, wherein the reduced coating has a general formula $A_{y-z}B_nO_x$;

wherein $y > z$; and

wherein $x' > x$.

8. The cermet catalyst material of claim 7 wherein the A metal particles are between 1 nanometer and 100 nanometers across and wherein the A metal particles are generally positioned at grain boundaries, grain surfaces and in intragranular pores.

9. The cermet catalyst material of claim 7 wherein x is between 3 and 7.

* * * * *