

Combustion Synthesis of Perovskite-type Metal Oxide Compound

Field of the Invention

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This invention relates to the combustion synthesis of perovskite-type metal oxide compound and refers particularly, though not exclusively, to such a synthesis of perovskite-type oxygen permeable materials using a combustion method where oxygen is introduced externally in the final stage to assist combustion

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Background of the Invention

Mixed ion electron conductive materials ("MIECM") have been under attention due to their potential application in solid oxide fuel cell, oxygen separation membranes and partial/selective oxidation of natural gas to produce syngas (hydrogen and carbon
15 monoxide). The production of syngas is a way to valorize natural gas, since this hydrogen rich gas mixture can be directly converted into electricity by solid oxide fuel cell ("SOFC") systems. Furthermore, syngas is a major intermediate for the production of both hydrogen and its downstream value-added chemicals, which are of growing
20 interest for both economic and environmental reasons. As a well-known MIECM, and due to its excellent stability, conductivity and structural versatility, ABO_3 structure perovskite-type materials have been studied extensively, from which a number of oxygen permeable materials have been developed. The potential application of oxygen permeable perovskite material in syngas production may eliminate the building
25 of a cryogenic oxygen plant, which may save up to 45% of the total investment cost and make it possible to compete with the traditional gas-reforming route.

Considerable progress has been made since Teraoka initiated systematic studies on oxygen permeabilities of ABO_3 perovskite materials by adjusting and substituting metal
30 ions on A or B sites. The highest oxygen permeation flux was found on $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$. However it was proved later the material has only limited mechanical and phase stability. Further studies showed that by doping Ba^{2+} in the A site, the perovskite structure stability is greatly improved without excessively impeding its oxygen permeation flux, and a stable 1000 h operation time was achieved on
35 $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ perovskite materials. Many other kinds of oxygen permeable perovskite materials that employ large varieties of constitutional elements such as La,

Ca, Cu, Ti, Bi, Zr, Ni, Mn and Ga etc have also been tested and exhibited considerable oxygen permeable properties.

Successful preparation of phase pure perovskite-type metal oxide compounds
5 demands an extensive mixing of constitutional metal elements to highest
homogeneity, no matter how many elements and whatever precursor are chosen. A
number of synthesis routes with the idea of highly mixing the constitutional elements
have been developed for the material preparations. The diversity includes several
representative methods such as solid-state reaction, gel casting, sol-gel, self-
10 propagation reaction, co-precipitation, hydrothermal crystallization and compound
decomposition.

The traditional ceramic route, namely, a high temperature solid-state reaction between
mechanically mixed metal oxides/carbonates has been used to fabricate the
15 perovskite materials. Generally, the starting materials in the oxide/carbonate form are
mixed together in the desired proportions by dry or wet ball milling. After milling, the
material is calcined and the resulting material is crushed and milled again. This
process can be further repeated to obtain additional homogeneity. Alternative methods
can also be used. These include using soluble metal salts instead of insoluble oxides.
20 Alternatively, organic polymers can be added to make a slip that undergoes a gel-
casting procedure. These give the further benefit of a higher homogeneity.

Another procedure involves co-precipitation. This method is to precipitate
simultaneously from a solution in either hydroxide or oxalate form to yield a precipitate
25 containing the correct proportions of constitutional elements. The precipitate is then
converted to a crystallized perovskite phase by heating to a desired temperature for a
given period.

The disadvantages of these methods are that they are time-consuming and not
30 contamination free. This is particularly so for solid-state reactions, and the co-
precipitation method, respectively.

The solid-state reaction methods may be improved to provide improved homogeneity,
and the co-precipitation method, may also be improved to remove excess alkaline
35 precipitating agents.

Another procedure involves the sol-gel method, which utilizes the high soluble properties of metal alkoxides in non-aqueous solvents to achieve a high level mixing of constitutional elements, and an additional hydrolyzing step must be incorporated into the process. There is another approach that utilizes the chelating and polymerization properties of organic ligands to realize a molecular-level mixing of elements and to avoid phase segregation. In practice, soluble inorganic metal salts (mostly nitrates) are dissolved together with soluble organic ligands (mostly citric acid or EDTA) to form a homogeneous aqueous solution. Using heat, water is gradually removed and the organic species start to polymerize while strongly chelating metal elements by their functional groups. The mixture solution gradually develops into a polymeric gel that has all the constitutional elements frozen in polymer lattice and in correct proportions. Subsequent heat treatment is required to burn off the organics to make the inorganic substance crystallize. Homogeneity is always better, and the "crystallizing temperature" is always lower, than the solid-state reaction route owing to the molecular level mixing.

Another method has employed synthesis by self-propagating combustion. When organic ligands are deliberately added to improve homogeneity and an appropriate organic ligands:metal nitrates ratio is achieved, the mixture can undergo a self-propagating combustion. This burns off all volatile organic compounds and leaves an amorphous or crystallized inorganic ash. Organic ligands serve both as a chelating agent that places metal atoms in highly disordered positions, and as a fuel that provides combustion energy for heat-induced crystallization. The ligands may be one or more of: glycine, urea, citric acid and cellulose, while the metal salts are, without exception, nitrates.

There are also combustion systems using one or more metal powders as the fuel. Potassium perchlorate may be used as an oxidant. This method may shorten the synthesis period and ease sample handling, but an additional purification step is inevitable.

Other methods include hydrothermal and compound decomposition. The hydrothermal method uses a highly alkaline aqueous solution as a crystallizing media in which all ingredients are added and well mixed until a hydrogel is formed. The hydrogel is then crystallized in an autoclave heated at 200°C or more. After induction and crystallization period the hydrogel transforms into perovskite product. However, due to great differences in hydrothermal stability and solubility in alkaline media, only limited

perovskite crystallization is successful. A compound decomposition procedure is used if all constitutional metal atoms happen to be incorporated into one heteronuclei complex, such as heteronuclei oxalate. By calcining the oxalate, a perovskite-type metal oxide compound is easily made. Unfortunately, the compound decomposition method is not an accepted method for the synthesis of numerous perovskite products.

In the self-propagating combustion method using multiple constitutional metal elements, it is always a concern that phase segregation may occur as a consequence of the different affinity between metal ions and organic ligands when the organic dosage is relatively low. In order to prevent metal ions from phase segregating before the burning-off takes place, sufficient chelating groups should remain. This may be achieved by increasing the dosage of organic ligands. As a result, the introduced metal nitrates are insufficient to fully oxidize the "fuel" and therefore the combustion transforms into a smoldering or frothing process. This results in a fluffy and sticky xerogel product. Also, due to its bulky and sticky nature, the xerogel product is not easily handled in the subsequent calcination process that burns off the voluminous polymeric bone to leave a fully developed perovskite structure. Introducing an extra oxidative supply (e.g. NH_4NO_3) may rebuild the proper oxygen balance and restore the self-propagating combustion, but it will also degrade the organic fuel well before a substantial polymeric framework forms, nor will it form a well crystallized perovskite phase.

Summary of the Invention

In accordance with a first preferred aspect there is provided a method of synthesizing perovskite-type metal oxide compounds, the method comprising:

- (a) forming an aqueous solution containing all required metal elements;
- (b) removing the aqueous media to form a gel precursor; and
- (c) combustion pyrolyzing the gel precursor in the presence of externally-supplied oxygen.

The externally-supplied oxygen may be supplied through a nozzle located above the gel precursor. The gel precursor is preferably a polymeric gel precursor.

The external supply of oxygen may be air, oxygen enriched air, or substantially pure oxygen; and may be supplied at a rate able to be controlled so as to control at least one of combustion reaction intensity, and the combustion reaction velocity.

After (a) but before (b) at least one soluble organic chelating agent may be added to the aqueous solution. Preferably, the combustion results in significant depletion of organic residuals. The soluble organic chelating agent may be one or more of:

5 ethylenediaminetetraacetic acid, citric acid, ammonium citrate, glycine, polyalcohol, polyamine and any soluble organics containing strong chelating functional groups. If the stable organic chelating agent lacks the ability to polymerize, a co-polymerization precursor may be added.

10 The metal elements may be one or more of: chlorides, sulfates, nitrates, citrates, acetates, alpha-hydroxycarboxylates, and inorganic and organic. The aqueous solution may be homogenous. During the formation of the gel precursor, resultant residual materials may be transformed into a foamy gel as a result of polymerization, and partial decomposition of the organic media.

15 Removal of the aqueous media may be by one or more of: evaporation by heating, distillation, and freeze drying. The foamy gel may be further heated to form the gel precursor. The external supply of oxygen may be started when combustion commences.

20 The prevoskite type metal oxide compounds may subsequently be calcined, pressed into at least one membrane, and the at least one membrane sintered.

25 According to a second preferred aspect there is provided a membrane produced by the above method; and a pervoskite-type metal oxide compound when prepared by the above method.

Brief Description of the Drawings

30 In order that the present invention may be fully understood and readily put into practical effect, there shall now be described by way of non-limitative example only preferred embodiments of the present invention, the description being with reference to the accompanying illustrative drawings.

35 In the drawings:

Figure 1 is a schematic view of a combustion synthesis apparatus;

Figure 2 is a schematic diagram of oxygen permeation test experimental set up;

Figure 3 is a room temperature XRD patterns showing phase development of samples prepared from different combustion-synthesis methods:

- (a) as-synthesized powder,
- 5 (b) calcined powder, 950°C, 5 hours
- (c) sintered discs, 1100°, 5 hours; the values after ECN indicate free oxygen: organic fuel molar ratio;

Figure 4 is a comparison of TGA/DSC profiles, between (a) the EDTA/Citrate/nitrates combustion sample and (b) the Complexation/Combustion sample;

- 10 Figure 5 shows SEM images of discs-shape membranes prepared from the EDTA/Citrate/Nitrate combustion and the Complexation/Combustion methods; and
- Figure 6 is a Comparison of oxygen permeation flux between the EDTA/Citrate/Nitrate combustion and the Complexation/Combustion methods. The volume of oxygen gas was standardized at 25°C at 1 atm.

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Detailed Description of the Preferred Embodiments

- Disclosed is a combustion method for preparing perovskite materials by making the metal-ligand xerogel combustible and using air and/or oxygen as an oxidant to boost
- 20 the subsequent combustion. In this way, a lower amount of, or even no, oxidative substance is present during gel condensation and polymerization. Therefore, the molecular-level mixed precursor gel structure is well preserved before combustion takes place. Once the gel is ignited, oxygen is supplied externally and continuously. This is useful in numerous perovskite-type metal oxide compounds preparation,
- 25 especially when multi-element or non-stoichiometric perovskite structures are required.

- The oxidative supply is provided externally by introducing a flow of continuous air, enriched air or pure oxygen from a nozzle to sustain and boost combustion of the
- 30 polymeric gel. This "freezes" or sets all the constitutional elements in the correct proportion for a desired perovskite structure. By pure oxygen is meant commercially available "pure" oxygen. This may not be 100% pure.

- By using a combination of the solid gel synthesis method and self-propagating
- 35 combustion synthesis to prepare a large variety of perovskite-type metal oxide compounds several advantages may result:

1. a large range of perovskite type metal oxides can be prepared as phase pure products generally without phase contamination;

2. the combustion process is more controllable as the oxidative supply that is used to burn-off the organic polymeric framework of the perovskite precursor gel is provided externally. By adjusting the external air/oxygen/enriched air/pure oxygen feeding rate, at least one of the combustion reaction intensity and velocity are able to be controlled to balance the need of perovskite production rate and the heat tolerance of the manufacturing facility; and

3. as the combustion is conducted in presence of a more than adequate oxidant supply, the produced product is significantly depleted of organic residuals. This assists in improving product purity and quality. Furthermore, there is a lowering of volume expansion of the precursor solution during evaporation since less bubbling takes place as a result of minor oxidative degradation. Therefore, a greater mass of perovskite products is able to be prepared per unit volume of a reaction vessel.

The process comprises three steps:

1. forming an aqueous solution containing all required metal elements;
2. removing the aqueous media to form a gel precursor for perovskite; and
3. combustion pyrolyzing the gel precursor in the presence of molecular oxygen, preferably supplied externally through a nozzle.

The first part of the process involves the dissolution of all constitutional metal salts in an appropriate solvent, preferably distilled or deionized water, to form a homogeneous solution. Varying soluble metal salts such as for example, chlorides, sulfates, nitrates, citrates, acetates, alpha-hydroxycarbonxylates, and inorganic and organic, may be used to prepare the mixed solution provided there is no precipitation during mixing. The types and amounts of all starting metal salts are determined by the composition of the desired perovskite phase. When the dissolution is complete, one or more soluble organic chelating agents are introduced to stabilize the metal ions to prevent precipitation. Most preferably, ethylenediaminetetraacetic acid, citric acid, ammonium citrate, glycine, polyalcohol, polyamine and any soluble organics containing strong chelating functional groups, may be used to form the stable metal-ligand complex. For organic ligands that lack the ability to polymerize, some co-polymerization precursor may need to be added.

The removing of the aqueous media in the second part of the process may be performed by any conventional procedure such as, for evaporation, distillation, freeze-

drying, and the like. The solution made in the first part becomes thicker upon condensing. Finally the resultant residual materials are transformed into a foamy gel as a consequence of polymerization and partial decomposition of the organic media. In order to make the gel combustible, it should be further heated to deplete excess
5 free solvent until a firm, black, charred gel is obtained.

As shown in Figure 1, the combustion pyrolysis of the third part of the process is preferably conducted in the same vessel 10 as that of the second part. If necessary, the charred gel 12 may be accumulated and relocated into another vessel. The vessel
10 10 material should be inert to the gel and air oxidation. Borosilicate glass "Pyrex", fused silica, quartz, alumina, zirconia, porcelain or porcelain enameled metal, and like materials may be used. Being heated from the bottom 14 by a hotplate 16, and/or more conveniently from its top surface by a gas torch, the charred gel 12 is easily ignited. Oxidative gas 18 (air, oxygen enriched air or pure oxygen) is applied
15 externally of the combusting, charred gel 12 by blowing through a nozzle 20 placed above the gel 12.

Combustion develops quickly from the igniting point and in minutes the gel 12 becomes red hot. After a period of 1 to 60 minutes, depending on the gel mass and
20 gas 18 flow rate, combustion will finish and yield an ashy product. Compared with conventional production methods, the combustion products are much more compact and non-sticky, it is also beneficial that the ashy products are more often better crystallized than conventional products. Improved oxygen permeation is also observed using the perovskite material made by this process.

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Example I

Perovskite-type metal oxide material preparation

This example is for a procedure for the synthesis of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ perovskite-type metal oxide compound and several comparative samples from known methods.

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$\text{Ba}(\text{NO}_3)_2$ (Merck, 99%), $\text{Sr}(\text{NO}_3)_2$ (Riedel-deHaen, 99%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Riedel-deHaen, 99%), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck, 99%), EDTA (EthyleneDiamineTetraaceticAcid, Lancaster, 99%), citric acid (Merck, 99.5%), glycine (Merck, 99.7%), glycerol (Lancaster, 99+%) and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25% wt, Merck)
35 were used as starting materials.

Required amounts of $\text{Ba}(\text{NO}_3)_2$ and EDTA powder were dissolved in an aqueous ammonia solution by stirring until the solution was clear. A fully dissolved aqueous solution containing required amounts of $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added resulting in a transparent and deep wine red solution. Citric acid was added and homogenized, transforming the mixture to an opaque brown-red suspension. A 25% aqueous ammonia solution was introduced drop-by-drop until a final pH of 6.5 was achieved. Then the suspension became a clear deep wine-red colour. The overall molar ratio of citric acid: EDTA: total metal was 3.0: 1.0: 1.0. No nitric acid or an excess ammonia solution was added. The solution was then heated in the beaker 10 on the hotplate 16 with the air supply nozzle 20 extended from the top, as shown in Figure 1.

As evaporation proceeded, the solution became viscous and deep black-brown. When the total volume had been reduced to one fifth of its initial volume, the solution started to froth and gradually changed to a foamy, black xerogel. Heating was continued to further char the gel, and to remove residual free water. The charred xerogel was then auto-ignited from the bottom. The air or oxygen supply 18 was initiated when combustion commenced so as to assist combustion. The xerogel combusted rapidly, and glowed incandescently. The combustion was completed within 15 minutes resulting in a black, powdery residual. This sample is subsequently preferred to as CC (complexation combustion) sample.

Four comparative samples, using the conventional (EDTA/citrate)/nitrate (ECN) combustion route with two different oxygen/fuel molar ratios, Glycine/nitrate (GN) and Glycerol/nitrate (GIN) combustion routes, were also made. The ECN samples have the same EDTA/citric acid/total metal ratio as the above-mentioned CC method, but additional NH_4NO_3 solid was introduced to make the free oxygen/fuel ratio at 0.46 or 0.70. For the GN and GIN samples, no extra NH_4NO_3 was added. The metal nitrates served as the sole oxygen donor, and the free oxygen/fuel ratio was kept at 0.50. No pH adjustments were made on the GN and GIN, except for the ECN sample. Once the solutions were made, they were evaporated on hotplates until almost all the free water was removed and auto-ignition began. The combustion reaction was completed in one minute for the ECN sample, while the GN and GIN samples completed the combustion in seconds.

Example II

Perovskite-type metal oxide materials characterization and evaluation

This example is of the procedure for making and characterizing disk-shaped membranes from perovskite powders produced according to the method of Example

- 5 1. If further considers an experimental set-up to test their oxygen permeabilities. TGA/DSC and SEM results are also furnished to give further explanation of some unique properties of the perovskite material made by the current invention.

- 10 All prepared powders from Example 1 were calcined at 950 °C for 5 hours and well mixed with 0.075 wt% methylcellulose binder after cooling. They were then pressed into disk-shaped membranes in a 16.0 mm i.d. stainless steel vacuumable pellet die set (International Crystal Lab) under 487 Mpa of isostatic ram pressure. The disc-shaped membranes were sintered in a box furnace (Lindberg Blue M) at 1100°C for 5 hours with a ramp rate of 2°C per minute. Before the permeation test, the disc-shaped
- 15 members were polished using 600-grit emery papers to have a 2.00mm consistency in thickness.

- 20 An oxygen permeation test was performed in a vertical split tube furnace assembled shown in Figure 2. The ceramic disc 20 was mounted on one polished end of inner quartz tube 21 by a ceramic sealant 22. Excess sealant 22 was used to fully cover the sidewall of the disc 20 to prevent any edge leakage. The effective inner permeation area of the disc was kept at 0.80 cm². Dried compressed air 23 at the rate of 70ml/min, and high purity helium (99.9995%) 24 at the rate of 30ml/min, were introduced into the upstream 25 and purge side 25 of the membrane, respectively.
- 25 The temperature was raised gradually from ambient to 850 °C and kept overnight. It was then cooled to 650 °C at the rate of 2 °C /min. After 30 min of stabilization, the effluent gas from purge side 26 was analyzed. Subsequent test points were performed at 50 °C step wisely with the same stabilization time as the first point and the final temperature being 900 °C.

- 30 X-ray diffractometer (Siemens, D5005) was used to identify the phase of as-synthesized powders and sintered discs. The as-synthesized powders' thermal gravimetric behavior was investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) in air (120ml/min) with heating rate of 10 °C
- 35 /min. Scanning electron microscopy was used to study the morphology of the sintered discs 20. Before imaging, the top surface of the discs was polished and sputter coated with gold. Before imaging a cross-section of the discs, no polishing was done.

Figure 3 shows the XRD patterns of the samples prepared from different combustion-synthesis methods for original powders, calcined powders and sintered discs, respectively. It can be seen from Figure 3 (a) that all as-synthesized powders share a common group of reflections at around 25 degree (two theta), which can be assigned as a mixed barium/strontium carbonate phase. At 35 degrees, the reflections indicate the presence of miscellaneous phases of mixed cobalt/iron oxide. The calcination of the as-synthesized powders made them crystallize towards the perovskite phase, with the CC sample showing the strongest reflection. Both the GIN and GN samples are the poorest at the perovskite main peak position, as shown in Fig.3 (b). The calcined powder of ECN-0.70 with an increased free oxygen/fuel ratio gave poorer crystallinity as compared to that with a lower free oxygen/fuel ratio (ECN-0.46). Calcined GIN and GN powders were not used to make discs due to their poor crystallinity. As shown in Figure 3 (c), after sintering at 1100 °C the disc 20 derived from the CC powder was better crystallized than those derived from the ECN powders. The XRD main peak intensity at 31.7 degree (2 θ) for the CC disc is 54 % and 450 % stronger than those of ECN-0.46 and ECN-0.70 discs, respectively. The ECN-0.70 disc was not chosen for the oxygen permeation test, as its mechanical strength was insufficient to withstand polishing. In contrast, the ECN-0.46 and the CC discs were quite solid and unbreakable.

A simple method way to mix constitutional elements thoroughly for a given perovskite synthesis is to dissolve the metal salts homogeneously in a solution. Unfortunately, phase segregation always occurs due to the different solubility and hydrolyzation rates of different metal ions when the solution is slowly heat condensed. By adding organic ligands that are rich in complexing groups (-OH, -NH₂, -COO-), the metal ions are captured and protected by the organic media to keep the metal ions in solution. As a result, the extent of phase segregation is minimized even if the solvent is completely removed. The more uniform the constitutional elements in as-synthesized powders, the less the diffusion barrier is for heat-induced perovskite crystallization.

The GIN and GN products' being poorly crystallized may result from an insufficient dose of organic ligands. For ECN samples, the loss of crystallinity and the rise of phase impurity may be attributed to the untimely oxidative attack on the organic ligands by NH₄NO₃. By comparing the ECN-0.70 with ECN-0.46 samples, it is found that the addition of increased amount of NH₄NO₃ results in more deterioration of succeeding phase crystallinity and purity of as-synthesized powers. However, higher

crystallinity and less phase contamination may be obtained if prepared by the CC route, as the oxidative source was brought in at the final stage externally and separately. This may maintain the ratio of free oxygen to fuel in the precursor solution at a minimum so as to make full use of the complexing nature of organic ligands. Meanwhile, the oxygen supply assisted combustion so as to burn-off substantially almost all organic residuals. It also helps to shrink the voluminous gel to a smaller volume that facilitates product treatment. For any other constitutional metal ions to be introduced to a designated perovskite structure, as long as they are able to be complexed by organic ligand-type polymer precursors, the CC route is applicable and advantageous in terms of sample treatment and product purity.

Figure 4 illustrates the DSC and TGA curves of the ECN-0.46 and CC as-synthesized powders. In general, two weight loss slopes were observed for both ECN-0.46 and CC powders in TGA curves. The first is around 400°C, which corresponds to a further pyrolysis of organic residuals. The second is located in the range 670~950°C and 630~850°C for the ECN-0.46 and CC powders respectively, corresponding to the decomposition of carbonates when the perovskite crystallization occurs to release CO₂. Compared with the ECN-0.46 sample, the first weight loss of the CC sample is lower (2% vs. 6%), which indicates that the CC method burns off organic residuals more efficiently. The process of the second step weight loss for the CC sample stops approximately 100°C earlier than that of the ECN-0.46 sample. This suggests that the CC powder releases bound CO₂ faster before it transforms into a final, stable perovskite phase. The thermal gravimetric behavior of the ECN-0.46 sample from 450 to 700°C, from the TGA curve shows a continuous weight gain. In addition, the ECN-0.46 and CC powders exhibit an exothermic DSC peak at 430 °C and 390 °C, respectively, which are in correspondence with their TGA results of the pyrolysis of organic residuals. When the temperature is increased, both show several endothermic peaks. For the crystallization of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} perovskite started at a temperature of 700°C by use of a modified citrate method, the emergence of perovskite phase and the decomposition of carbonates happen somewhat simultaneously within the range of 700 ~ 950 °C for the ECN-0.46 and CC samples. The more pronounced endothermic peak for the CC sample at 838°C may accounts for its higher extent of crystallinity. The endothermic peaks above 900°C correspond to further structure development of the CC and ECN-0.46 perovskite phases.

The SEM images of disc-shape membranes made from the ECN-0.46 and CC powders are shown in Figure. 5. For Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} membranes, it is believed

that larger primary grain size and fewer grain boundaries are beneficial to oxygen permeation since oxygen ions move faster in the bulk than the interface. It can be seen from Figure 6 that the CC membrane has fewer and smaller pinholes and less surface discontinuity. This generates less grain boundaries and reduces diffusion obstacles for oxygen transportation compared to the ECN-0.46 membrane. As a result, the CC membrane possesses a higher oxygen flux.

Figure 6 shows the oxygen permeability of disc-shape membranes made from the ECN-0.46 and CC powders. Within the temperature range indicated, the CC membrane showed better oxygen permeation. At 850°C, the oxygen flux of the CC membranes is 0.93ml/cm².min, which is about 20 % higher than that of the ECN-0.46 membrane.

Perovskite-type metal oxide compound materials have impact on oxygen production technology and oxygen-involved industrial processes. Due to its infinitive permselectivity to oxygen, the MIECM (mixed ion electron conductive material) type perovskites that are able to be made by the present invention are able to fabricate dense ceramic membranes for oxygen production from air. They may also be used to fabricate high-surface-area hollow-fibre membrane reactors for partial oxidation of natural gas or light hydrocarbons. Ceramic hollow fibre membrane reactors are a very promising technique since it combines oxygen separation and partial oxidation of light hydrocarbon (mostly methane, from natural gas) in one reaction, thereby eliminating the building of a costly oxygen plant if an autothermal syn gas (carbon monoxide and hydrogen) manufacturing facility is to be built. Syn gas is later converted to gasoline or hydrogen, or other value-added chemicals.

Convenient production of various functionalized perovskite ceramic materials that are used as SOFC (solid oxide fuel cell) electrode material, dielectric and piezoelectric material for capacitors, oscillators, filters and energy transducers in electronic industry and the related field may be enhanced.

This method described above offers the advantages of facilitating the preparation and crystallization of perovskite-phase structures. The CC method yields perovskite products with minimum phase contamination and the high crystallinity. Additionally, the oxygen permeation tests and SEM studies reveal that the disc-shaped membranes made from the CC powders exhibit fewer structural defects and higher oxygen permeation flux.

Whilst there has been described in the foregoing description preferred embodiments of the present invention, it will be understood by those skilled in the technology concerned that many variations or modifications in details of design or construction
5 may be made without departing from the present invention.

THE CLAIMS

1. A method of synthesizing perovskite-type metal oxide compounds, the method comprising:
 - (a) forming an aqueous solution containing the required metal elements;
 - (b) removing the aqueous media to form a gel precursor; and
 - (c) combustion pyrolyzing the gel precursor in the presence of externally-supplied oxygen;wherein the externally-supplied oxygen is supplied through a nozzle located above the gel precursor, and the gel precursor is a polymeric gel precursor.
2. A method as claimed in claim 1, wherein the external supply of oxygen is selected from the group consisting of: air, oxygen enriched air, and substantially pure oxygen.
3. A method as claimed in any one of claims 1 to 2, wherein externally-supplied oxygen is supplied at a rate able to be controlled so as to control at least one of reaction intensity, and the combustion reaction velocity.
4. A method as claimed in any one of claims 1 to 3, wherein after (a) but before (b) at least one soluble organic chelating agent is added to the aqueous solution.
5. A method as claimed in claim 4, wherein the combustion results in significant depletion of organic residuals.
6. A method as claimed in claim 4 or claim 5, wherein the soluble organic chelating agent is one or more of: ethylenediaminetetraacetic acid, citric acid, ammonium citrate, glycine, polyalcohol, polyamine and any soluble organics containing strong chelating functional groups.
7. A method as claimed in any one of claims 4 to 6, wherein if the stable organic chelating agent lacks the ability to polymerize, a co-polymerization precursor is added.
8. A method as claimed in any one of claims 1 to 7, wherein the metal elements are inorganic and/or organic and selected from the group consisting of: chlorides, sulfates, nitrates, citrates, acetates, alpha-hydroxycarboxylates.

9. A method as claimed in any one of claims 1 to 8, wherein the aqueous solution is homogenous.
10. A method as claimed in any one of claims 1 to 8, wherein during the formation of the gel precursor resultant residual materials are transformed into a foamy gel as a result of polymerization, and partial decomposition of the organic media.
11. A method as claimed in any one of claims 1 to 10, wherein removal of the aqueous media is by one or more of: evaporation by heating, distillation, and freeze drying.
12. A method as claimed in claim 10, wherein the foamy gel is further heated to form the gel precursor ready for combustion pyrolysis.
13. A method as claimed in any one of claims 1 to 12, wherein the external supply of oxygen is started when combustion commences.
14. A method as claimed in any one of claims 1 to 13, wherein the pervoskite type metal oxide compounds are subsequently calcined, pressed into at least one membrane, and the at least one membrane sintered.
15. A membrane produced by the method as claimed in any one of claims 1 to 14.
16. A pervoskite-type metal oxide compound when prepared by the method of any one of claims 1 to 13.