Final Report

LOW TEMPERATURE CATHODE SUPPORTED ELECTROLYTES

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Submitted by

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1.0: ABSTRACT

This report represents a summary of the work carried out on this project which started October 1999 and ended March 2003. A list of the publications resulting from the work are contained in Appendix A.

The most significant achievements are:

1) Dense nanocrystalline zirconia and ceria films were obtained at temperatures < 400°C.
2) Nanocrystalline films of both ceria and zirconia were characterized.
3) We showed that under anodic conditions 0.5 to 1 micron thick nanocrystalline films of Sc doped zirconia have sufficient electronic conductivity to prevent them from being useful as an electrolyte.
4) We have developed a process by which dense 0.5 to 5 micron thick dense films of either YSZ or ceria can be deposited on sintered porous substrates which serve as either the cathode or anode at temperatures as low as 400 °C.
5) The program has provided the research to produce two PhD thesis for students, one is now working in the solid oxide fuel cell field.
6) The results of the research have resulted in 69 papers published, 3 papers submitted or being prepared for publication, 50 oral presentations and 3 patent disclosures.

2.0: INTRODUCTION

During the last several years, much of our research activities on solid oxide fuel cells (SOFCs) have been focused on developing the trilayer SOFC structures which have dense 1-5 micron thick zirconia (electrolyte) layers on porous (anode or cathode) substrates.The majority of the researchers who are trying to achieve this configuration have been attempting to build the trilayer by co-sintering the electrolyte with the anode and subsequently screen printing (and sintering) the cathode onto the electrolyte. It is obvious that this approach has fundamental limitations because shrinkage of the layers and chemical reactions between the layers can not be avoided at high sintering temperature.

Two possible directions have been identified as a potential ways to solve these problems. One of the directions is to decrease the particle size in the powder, which allows lower processing temperatures. We did some investigations in this direction [1-5] and found that this approach works, but these improvements are limited and does not completely solve the problem.

Another direction is to use solution deposition techniques and metal organic polymers as precursors. Since earlier we had developed a polymer precursor process which allowed the formation of 0.1 to 1 micron thick dense nanocrystalline zirconia films on smooth, dense substrates at temperatures below 800°C [6-7], we have focused on using this technology as the method to produce the required dense 1-5 micron thick electrolyte layers on either pre-sintered porous cathode or anode substrates at processing temperatures < 800°C. As it turns out, due to the surface roughness and open porosity of the substrate, our process for making dense films on dense substrates does not transfer without fundamental modification.

As a result, efforts have been initiated to modify the polymer precursor process. The process which has evolved combines powder processing with the polymer precursor process to

yield what we call the net-shape process. The idea of this new approach is based on two-step process. The function of the first step is to prepare a net-shape green body from the powder using low temperature sintering or even no sintering at all. The function of the second step is to densify this green body using metal oxide polymer. This allows the use of low temperatures and densification of the material will be achieved without shrinkage.

Using this process, we have been successful in making 1-10 micron thick dense zirconia layers on either the porous anode or cathode. This allows formation of the desired trilayer structures for the SOFCs. However the potential of net-shape processing is much greater than making simple electrolyte structures. It does not have limitations in the thickness of the coating or processing temperature in contrast to other technologies. It allows the development of new types of materials with precisely controlled porosity and composition, composite materials from the elements which are not compatible, and deposition of ceramic coatings on a much wider range of materials (such as metals). In fact, this process is equivalently applicable to irregular as well as flat surfaces, so application areas can be substantially extended.

3.0: EXECUTIVE SUMMARY

Final Report April 1, 2000 to March 31, 2003

This program was designed to exploit some of the polymer precursor technology which had been developed in previous DOE and Gas Research Institute projects to produce the trilayer SOFC structures which have dense 1-5 micron thick zirconia (electrolyte) or ceria layers on porous (anode or cathode) substrates. The majority of the researchers who are trying to achieve this configuration have been attempting to build the trilayer by co-sintering the electrolyte with the anode and subsequently screen printing (and sintering) the cathode onto the electrolyte. It is obvious that this approach has fundamental limitations because shrinkage of the layers and chemical reactions between the layers can not be avoided at high sintering temperature.

In our previous studies we had developed polymer precursor processing to make oxide films and in the ***1st Task of this program: Thin Film Studies:Nanocrystalline Electrolyte***; we showed that we could make dense nanocrystalline zirconia and ceria films at temperatures as low as 400°C. These were significant achievements, but the success was limited to deposition on smooth, dense substrates and with film thicknesses < 1 micron. The results were helpful, but did not allow us to prepare the 1-5 micron thick dense electrolyte on macroporous electrode substrates which is required for the successful development of the trilayer structure of the SOFC.

The ***2nd Task of this program: Preparation of Graded Porous Substrates*** was the vehicle we used to develop the technology required to prepare 1-5 micron thick dense electrolyte films on macroporous substrates at temperatures <800°C. With the assistance of NexTech, we were able to develop sintered macroscopic LSM cathodes which could be used as substrates for our electrolyte film. We initially attempted to use the solution deposition technique which we had developed previously which allowed the formation of 0.1 to 1 micron thick dense nanocrystalline zirconia films on smooth, dense substrates at temperatures below 800°C to produce the required dense 1-5 micron thick electrolyte layers on the pre-sintered porous cathode. As it turns out, due to the surface roughness and open porosity of the substrate, our process for making dense films on dense substrates does not transfer without fundamental modification.

As a result, efforts were initiated to modify the polymer precursor process. The process which evolved combines powder processing with the polymer precursor process to yield what we call the *net-shape process*. The idea of this new approach is based on a two-step process. The function of the first step is to prepare net-shape green body from the powder using low temperature sintering or even no sintering at all. The function of the second step is to densify this green body using metal oxide polymer. This allows the use of low temperatures and densification of the material will be achieved without shrinkage. *(a patent disclosure has been filed.)*

Using this process, we have been successful in making 1-10 micron thick dense zirconia layers on either the porous anode or cathode. This allows formation of the desired trilayer structures for the SOFCs. However the potential of net-shape processing is much greater than making simple electrolyte structures. It does not have limitations in the thickness of the coating or processing temperature in contrast to other technologies. It allows the development of new types of materials with precisely controlled porosity and composition, composite materials from the elements which are not compatible, and deposition of ceramic coatings on a much wider range of materials (such as metals). In fact, this process is equivalently applicable to irregular as well as flat surfaces, so application areas can be substantially extended.

4.0: RESULTS AND DISCUSSIONS

Examples of the results of our processing to obtain planar structures of real materials are discussed in the following and can be found in several publications (see for example [8-11]). Several examples from our investigation can illustrate these unique features of this approach.

1. Dense yttrium stabilized zirconia (YSZ) coatings.

A slurry containing YSZ particles was deposited on a sapphire substrate using spin coating and dried to form the initial porous body of the film. It was backfilled several times by YSZ polymer with subsequent annealing at 400^{o}C to remove the organic content. The final result was a transparent, dense YSZ coating. SEM cross-section of this coating is shown in Fig.1a. It was possible to anneal this coating at elevated temperatures without cracking or changes in transparency. The result of annealing at 900^{o}C is shown in Fig.1b.

The results of electrical testing are shown in Fig.2 (conductivity as a function of annealing temperature) for the sample prepared by net-shape processing in comparison with the samples prepared by other techniques (tape cast powder based sample and a sample prepared by polymer precursor deposition technique). It can be seen that all three samples have the same maximum conductivity, but annealing temperatures required to achieve this conductivity are quite different (1300^{o}C for the powder based sample, 900^{o}C for the polymer derived sample and less than 500^{o}C for the net-shape processed sample).

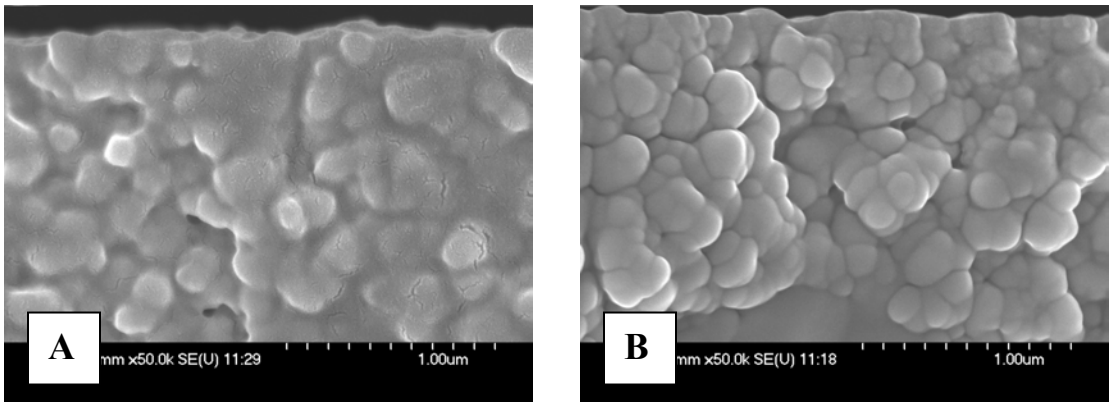

Fig.1. SEM pictures of cross-sections of dense YSZ coating on sapphire prepared using net-shape processing.
A – as prepared at 400°C; B – after annealing at 900°C.

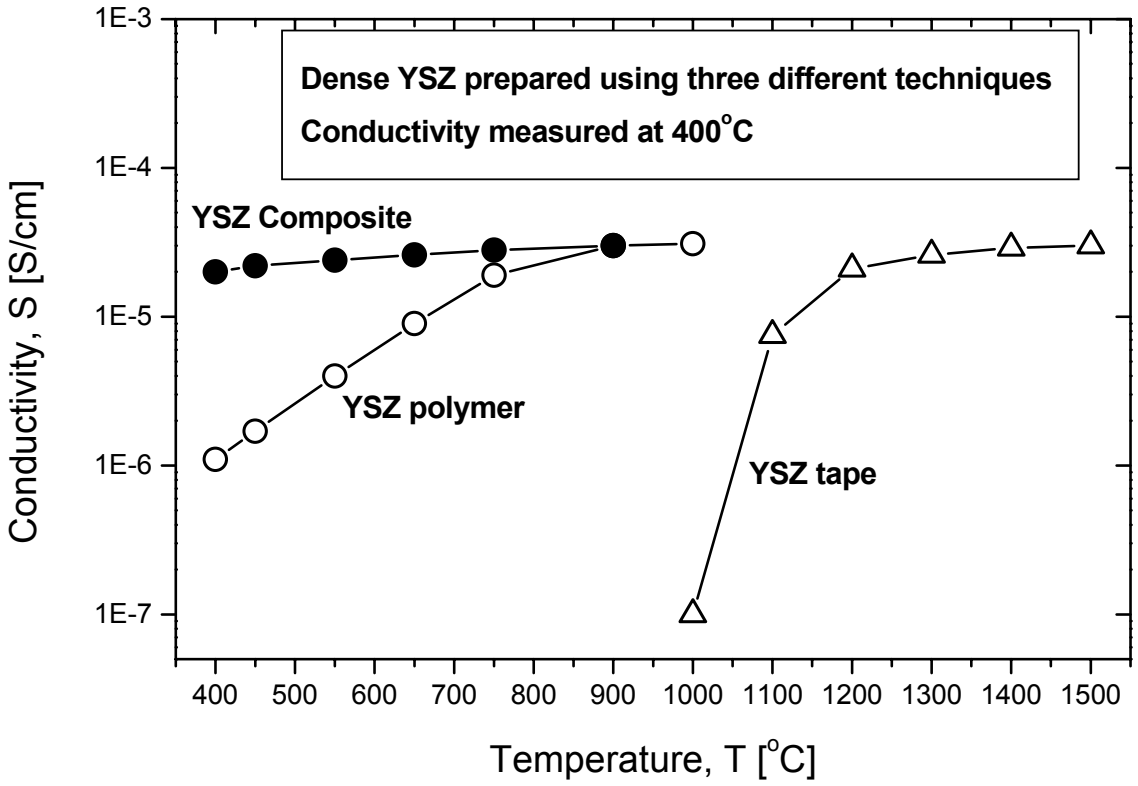

Fig.2. Comparison of the properties of YSZ prepared three different techniques: Tape casting at sintering (YSZ tape); Chemical deposition (YSZ polymer); and net-shape processing (YSZ composite).

2. Dense ceria – zirconia composite films.

The same YSZ slurry, substrates and deposition technique were used to prepare the initial green coating. The difference was in the backfilling polymer. Gadolinium doped ceria polymer was used instead of YSZ polymer. SEM photographs of the cross-sections are shown in Fig.3. Fig.3a shows the initial porous YSZ coating (before backfilling) and Fig.3b the final ceria-zirconia composite (after backfilling by ceria polymer). It is seen from the figure that net-shape processing allows the preparation of dense composite materials starting from an initially porous green body. Studies of the electrical properties of these zirconia composite films show that the electrical conductivity of the composites obtained at 400 °C are equivalent to zirconia which has been processed at high temperatures. (see Appendix B)

For more details on the net shape process, see Appendix C.

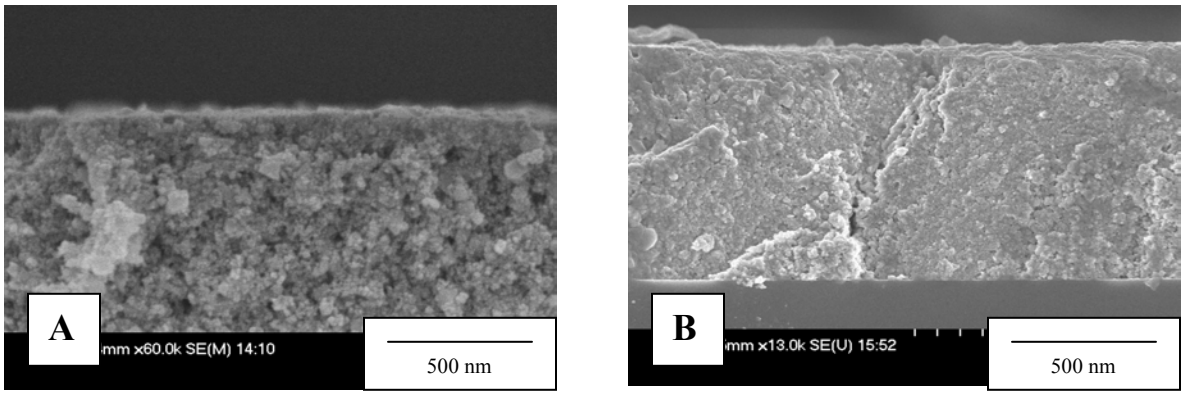

Fig.3. Ceria-zirconia composite coating on sapphire prepared using net-shape processing. A – Net-shape YSZ green body; B – Final ceria-zirconia composite.

3. Nickel –YSZ cermet.

The same YSZ slurry, substrates and deposition technique were used to prepare the initial green coating. The difference was in the backfilling polymer which was a nickel polymeric precursor.

The temperature dependence of the conductivity is shown in Fig.4a for a Ni-YSZ cermet prepared by this way. The down triangles correspond to initial state of cermet (with oxidized Ni) measured in air. The up triangles correspond to the reduced state of the cermet (with metallic Ni) measured in forming gas. This experiment shows that good connectivity was achieved in the Ni phase.

Fig.4b shows the stability of the cermet during reduction and oxidation. It can be seen that after some changes in the conductivities of NiO and Ni during the first three cycles the composite is very stable.

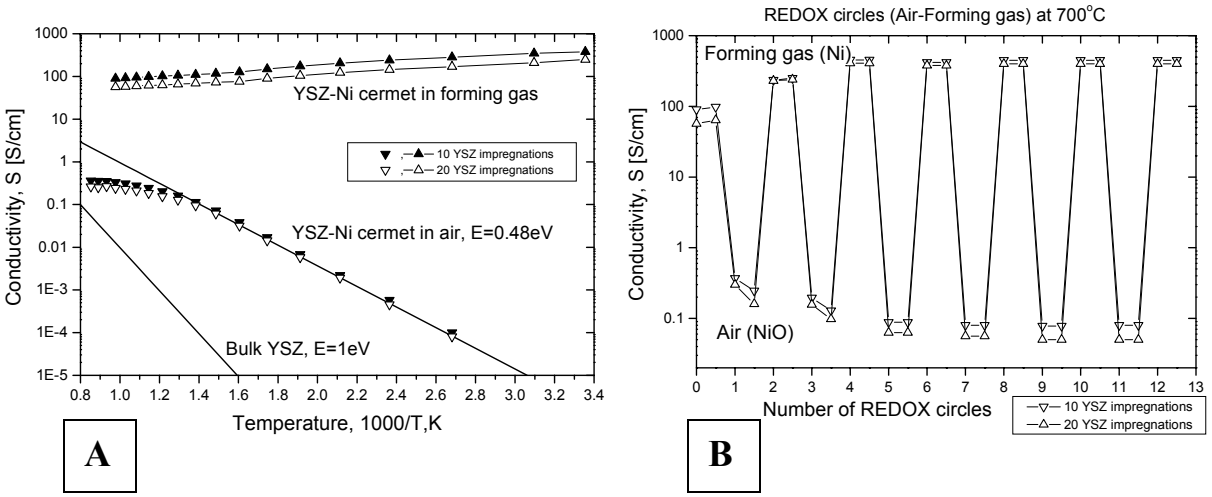

Fig.4. Electrical properties of Ni-YSZ cermet prepared using net-shape processing. A – Temperature dependence of the conductivity in oxidized and reduced state; B – Stability at the REDOX circles.

4. Mixed conducting compositions.

Samarium strontium cobaltite (SSC) polymer was used for the backfilling of a YSZ green ceramic layer to prepare a mixed conducting composite coating. Fig.5 shows the temperature dependence of the electronic conductivity for two samples with different SSC/YSZ ratios (down and up triangles) in comparison with pure SSC (circles) and ionic conductivity of YSZ straight line. It can be seen that the temperature dependence of the conductivity for composite samples is similar to pure SSC, so it is controlled by the electronic conductivity of SSC.

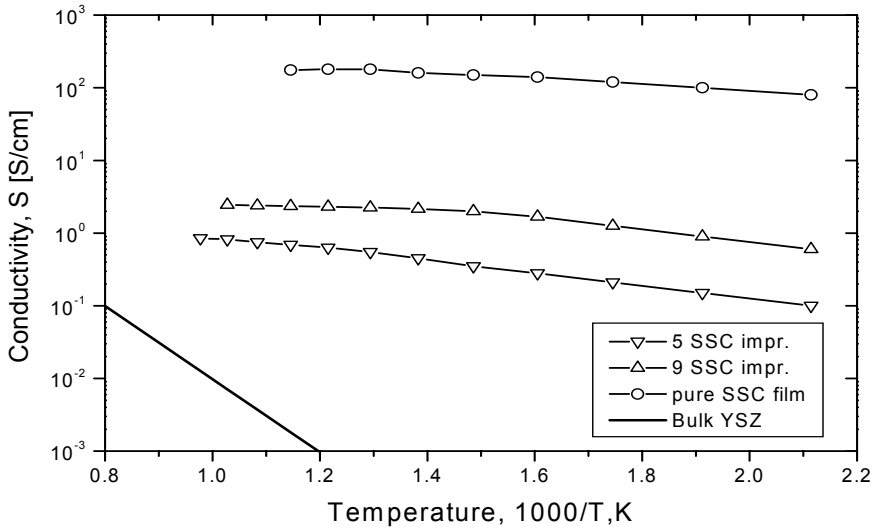

Fig.5. Mixed conducting YSZ-Samarium strontium cobaltite (SSC) composition prepared using net-shape processing. Temperature dependence of the conductivity for pure SSC coating and two YSZ-SSC composites with different YSZ/SSC ratios.

5. Titanium dioxide as an example of dense bulk materials.

Bulk unsupported sheets (thickness 0.7mm) were prepared from TiO_2 powder using tape casting and lamination. They were pre-annealed at 1100^{o}C to achieve an initially porous ceramic material and backfilled by titanium polymer to obtain a dense TiO_2 structure.

Fig.6 clearly shows possibility of densification of bulk materials by net-shape processing.

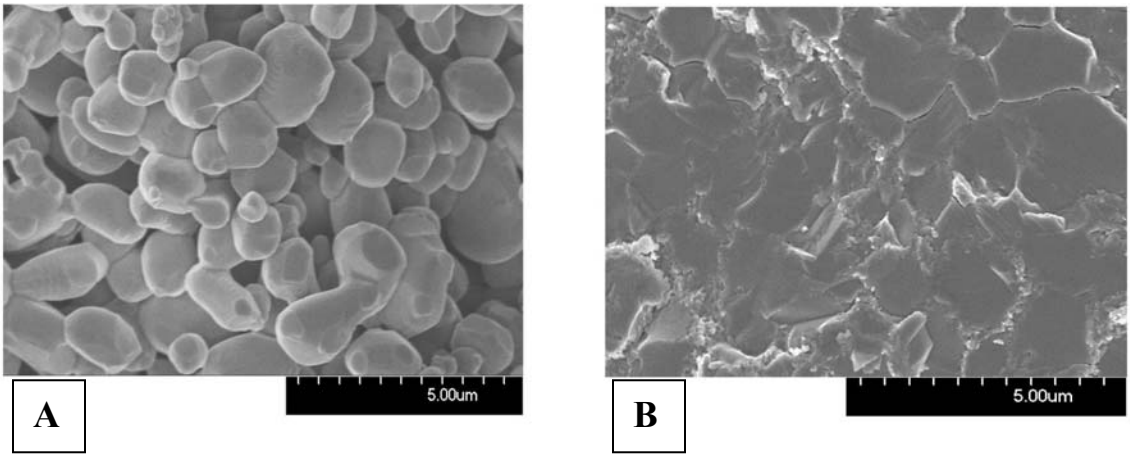

Fig.6. SEM photographs of the cross-sections. Bulk TiO2 sheet (thickness 0.7mm). A – Initial net-shape porous body (before backfilling); B – Final product (after backfilling and annealing at 900^{o}C).

5.0: CONCLUSIONS

It is apparent from the examples given above that the process which was developed in this program has importance beyond the preparation of trilayers for SOFCs. This process opens up the possibility of the net-shape formation of ceramic materials. (particularly for 2 dimensional structures) In addition it opens the possibilities for preparation and investigation of nanocrystalline materials. It includes the preparation of thin to thick nanocrystalline coatings and bulk nanocrystalline materials and using the same technological procedure the preparation of new types of nanocrystalline composite materials with precise control of the composition and porosity, etc. Some of the important features of this net-shape process are: low processing temperature (such as 400^{o}C), elimination of the shrinkage at all stages of the material preparation, possibility to control porosity and composition of the final material and opportunity to build composite materials from the components which are not compatible otherwise (due to reaction, interdiffusion at elevated temperatures, significant difference in the sintering temperature, etc.).

Low processing temperature is important, in particular if the grain size of the ceramics (or some components of the composite material) need to be maintained in the nanosize range. Hot pressing technique allows preparation of nanocrystalline bulk materials, but has difficulties with deposition of thin supported films and irregular shaped objects [12-14]. Physical and chemical

deposition techniques allow the preparation of thin nanocrystalline coatings [15-20], but the thickness of the coatings is usually limited to < 1μm. Both of these techniques fail if the components of the composite material should have significantly different grain size. This approach allows the preparation of coatings of any thickness as well as bulk materials using the same technological procedure and has no problem with composite materials.

Elimination of the shrinkage is important for thicker coatings (with the thickness greater than 1μm), bulk and irregular shaped ceramic, because shrinkage will cause cracking and delamination. This approach gives the unique possibility to overcome these problems and to deposit layers of any thickness (from submicron to millimeter range).

The possibilities to control porosity and composition of the material are other unique features of this approach, because of separation the stages of net-shape body formation and densification by backfilling in a two-step process. It allows controllable densification of the material (from ~50% porous initial body up to dense material) and controllable changes the composition by using different backfilling metal organic polymers.

The opportunity to build composite materials from the components which are not compatible otherwise is connected with the low processing temperature, which minimizes chemical reactions or interdiffusion. Several existing technologies allow preparing material at low temperature, but none of them are capable of both controlling porosity and grain size in these systems.

Examples of the practical importance of this approach can be illustrated (but not limited) as follows.

1. Low processing temperature and elimination of the shrinkage allows preparation of thin film ferroelectric capacitors using thin metal foils as substrates. New types of energy storage products can be generated by this approach. For example distributed capacitors for circuit board application, multilayer capacitors with very low series resistance, etc.
2. Ionic and mixed conductive ceramics are used in a number of elements of different energy conversion devices (such as solid oxide fuel cells, solid state gas reformers, etc). The basic elements of these devices are multilayer systems of ionic and mixed conductive single phase and composite materials [21-22]. Exact control of porosity and composition has crucial importance for these systems and net-shape processing has a potential for significant improvement of these properties. Net-shape processing can be efficiently used for production of different layers of these systems or the entire multilayer structure.

Different ceramic and composite coatings are used for protection of the metal surfaces from oxidation, corrosion and overheating. An example is YSZ coatings on different elements of gas turbines [23]. Thermal-spray and EB-PVD technologies are efficiently used for this purpose. Net-shape processing has a potential for significant improvement of the properties of such type of coatings, because the structure and the composition of the coating can be optimized. New types of thermal-barrier coatings can be developed by incorporation different additional elements in the coatings including metals and metal oxides to improve

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7.0: APPENDICES

Appendix A

Papers published, papers presented, oral presentations related to this program

1. S. Thevuthasan, S. Azad, O.A. Marina, V. Shutthanandan, D.E. McCready, L. Saraf, C.M.Wang, I. Lyubinetsky , C.H.F. Peden, V. Petrovsky, *Influence of Multiple Interfaces on Oxygen Ionic Conductivity in Gadolinia-Doped Single Crystal Oxide Electrolyte Multi-Layer Nano Films*, presented on IEEE Fuel Cell Conference (2003) – to be published.
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Appendix B

ELECTRICAL PROPERTIES OF YTTRIA STABILIZED ZIRCONIA FILMS PREPARED BY NET SHAPE TECHNOLOGY

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Keywords: net shape technology, yttria stabilized zirconia, polymer precursor, colloidal suspension, impedance spectroscopy.

ABSTRACT

The preparation of dense electrolyte films for most electrochemical devices is a crucial technological process. Net shape technology is a new approach, which uses a combination of colloidal suspensions and polymer precursor techniques, to obtain the dense electrolyte layers. It allows the overlapping of the thickness range from 1 to 10 μm in which other preparation techniques experience difficulties. Net shape processing is a low temperature technology (preparation temperature can be as low as 400^{o}C) and it eliminates shrinkage of the film during the densification stage, so chemical reactions between the substrate and the film can be minimized. In this study two types of dense substrates were used to confirm these features of the net shape technology: single crystal sapphire and platinum foil. It was shown that dense yttria stabilized zirconia (YSZ) layers can be obtained on both types of substrates at the temperatures as low as 400^{o}C. Moreover, further higher annealing temperature does not produce either shrinkage or cracking of the film. Electrical properties of YSZ films were measured in plane (on sapphire) and through the film (on platinum) using impedance spectroscopy and two-probe DC methods.

INTRODUCTION

Solid oxide fuel cells (SOFCs) are one of the most efficient energy conversion devices [1]. The main demand in the current SOFC development is lowering operation temperature to the range of 600˚C – 800˚C. In order to lower operational temperature and increase or at least sustain performance comparable to that at high temperature SOFCs, it is necessary to decrease the resistance of the electrolyte. One of the ways to achieve this goal is to decrease the thickness of the electrolyte.

Yttria stabilized zirconia (YSZ) is the most commonly used material as SOFC electrolyte and several deposition techniques have been used to develop thin film YSZ on either the anode or cathode. The methods include chemical and physical deposition, such as Electrochemical Vapor Deposition (EVD) [2] or magnetron sputtering [3], and liquid precursor and powder processing techniques such as polymer spin coating [4] or tape casting [5]. The detailed description of YSZ thin film fabrication techniques can be found in the review article [6]. All of these techniques experience difficulties with deposition of 1 to 10 μm thick electrolyte layers. Powder based techniques (such as tape casting, screen printing, etc.) are cost effective, but they have limitations in case of thin layer deposition. Moreover, the required high temperature co-sintering of the

electrode and electrolyte limits application of these techniques to anode supported SOFCs because of chemical reactions between cathode and electrolyte during high temperature sintering of cathode supported SOFCs. In contrary to powder based techniques, polymer technologies limit the thickness of one deposition to ~100 nm. During deposition of thicker layers shrinkage connected with decomposition of organic compounds causes cracking of the film. In addition, film thickness of 1 μm seems to be the upper limit even for multiple depositions. In general, chemical and physical deposition techniques allow deposition of dense YSZ layers at low temperature, but the cost of such kind of processing is too high for widespread applications.

The aim of this research was to develop a low temperature method for deposition of 1 to 10 μm thick YSZ electrolyte using a combination of YSZ powder and YSZ polymeric precursor (net shape processing) [7]. In this process the powder is first deposited onto the surface to provide a framework of connected particles into which the polymeric precursor impregnates to form an oxide particle / organic polymer composite film. Upon heating to 300˚C, the polymer decomposes to yield a nanocrystalline layer of YSZ, which fills the space between the particles, so dense material can be prepared without shrinkage during further annealing. The goal of the research was to show the possibility of depositing dense electrolyte layers at low temperature using net shape processing, to investigate structural stability of these layers at elevated temperatures and to compare the resulting electrical properties with those obtained for YSZ electrolytes prepared by commonly used techniques (high temperature sintered bulk ceramics).

EXPERIMENTAL

The YSZ ($Zr_{0.84}Y_{0.16}O_x$) films were prepared on platinum and sapphire substrates by net shape technology, which combines colloidal suspension and polymer precursor techniques. The colloidal suspension was prepared using commercially available YSZ powder (Zirconium Sales of America Inc.) with an initial grain size of about 100nm, while the YSZ polymer was prepared using zirconium chloride and yttrium nitrate precursors (Alfa Aesar). The ratio between YSZ powder and polymer precursor controls the final porosity of the material. Dense material can be prepared if this ratio is equal to 1:1. The materials with controlled porosity can be also prepared using higher ratios of powder to polymer. One of these compositions (ratio of 5:1) was investigated as well. This study focuses on the dense films with thickness in the range 1 to 3 μm range.

Scanning Electron Microscopy (SEM) images were obtained using a Field Emission Scanning Electron Microscope Hitachi S-4700, while the Atomic Force Microscopy (AFM) images were obtained using a Scanning Probe Microscopy Digital Instruments Nanoscope IIIa. Two probe DC measurements were performed using a Keithley Electrometer 6517A. The DC results were confirmed by two probe impedance spectroscopy, which were performed using a Dielectric Interface Solartron 1296 together with an Impedance Gain Phase Analyzer Solartron 1260 (in-plane measurements). The measurements through the film were performed using a Battery Tester Solartron 1470 and Impedance Gain Phase Analyzer Solartron 1255.
Silver paste (ESL 129C) contacts were used for the in-plane (YSZ films on sapphire substrate) electrical measurements. Platinum paste (ESL 5542) was used for the top contact deposition for the measurements through the film (YSZ on platinum foil substrate). These samples were pre-

annealed at 800°C for 2h and re-annealed at the same temperature after the deposition of the top contact.

RESULTS AND DISCUSSION

Dense YSZ coatings (powder and polymer ratio of 1:1) appear to be transparent after deposition (annealing temperature 400°C). Porous YSZ coatings (powder and polymer ratio of 5:1) were semitransparent. The coatings on both sapphire and platinum substrates were free of cracks as they were initially made and after the further high temperature annealing (up to 1000°C).

The microstructure of fracture cross section of the coatings was examined by SEM. The results of this investigation are summarized in Figures 1 and 2. The images of the cross-sections for the films on the sapphire are presented in Figure 1. Figure 1a shows dense YSZ coating (powder and polymer ratio of 1:1) as prepared (after annealing at 400°C). Two types of grains are observable in this coating: grains of about 100 nm derived from the YSZ powder which forms the framework and 10nm nanocrystalline YSZ, which originates from the polymer decomposition and fills the space between these grains. When the annealing temperature was increased, the nanocrystalline grains crystallized and created a uniform microstructure. After annealing at 900°C (Figure 1b) the crystallization process is completed and only 100 to 200 nm grains are visible. The important feature is that this recrystallization occurs in a dense structure (more than 95% of theoretical density) so shrinkage did not occur. Similar processes take place in the case of porous YSZ coating (powder and polymer ratio of 5:1). The only difference is the amount of nanocrystalline YSZ derived from the polymer is not sufficient to fill all space in the initial YSZ framework having a porous ceramic material with well developed connection between particles (Figure 1c). This type of material can not be used as oxygen separation membrane because it has open porosity, but it can be useful as the YSZ skeleton for the electrodes, because it has high effective surface area for exchange with the gaseous phase.

Figure 2 shows a SEM image of a cross section and AFM image of the surface of the dense YSZ film produced (powder and polymer ratio of 1:1) on platinum foil. It can be seen from the cross-section SEM image (Figure 2a) that the film is well attached to the platinum substrate, with no open porosity and looks similar to the coating on sapphire. An important feature of the net shape processing is the ability to planarize rough surfaces (in our case platinum foil). The coating completely covers the relief of the platinum foil and provides a smooth and glossy surface. The grain size of the polymer derived nanocrystalline YSZ is the only source of the final roughness which can be seen in the AFM image (Figure 2b). The value of this grain size estimated from the AFM image is 50nm after annealing YSZ film at 800°C.

It is possible to conclude from the microstructural investigation that net shape processing allows the deposition of dense YSZ coatings on the dense substrates at temperatures as low as 400°C. The question remains are the electrical properties as those of bulk YSZ ceramic material? In order to answer this question the electrical properties of the film were determined using impedance spectroscopy and two probe DC measurements.

A sapphire is a dielectric substrate, so in plane measurements are used to investigate the electrical properties of these structures (see Figure 3a). The small electrode resistance in

comparison with the resistance of the material is an advantage in the case of thin films measurements. However, it is impossible to separate the impact of grain and grain boundaries resistances from the material resistance because of the influence of sample holder capacitance. The value of the sample holder capacitance in our case was $5*10^{-12}$ F which is four orders higher than the estimated grain boundary capacitance ($5*10^{-16}$F). Therefore only one semicircle should be visible in the impedance spectra and it should correspond to the overall resistance of the material ($R_g + R_{gb}$). The electrical equivalent circuit for this measurement is presented in Figure 3b. The elements of the equivalent circuit are represented by resistance of the grain and grain boundary $R_g + R_{gb}$ and geometrical capacitance C_{geom}, which consists of the sample and sample holder capacitance, capacitance of cables and input capacitance of electronic instrument. A typical impedance spectrum resulting from YSZ film on sapphire is presented in Figure 3c. The spectrum consists of one semicircle, which confirms the negligible influence of the electrode resistance and allows investigation of the total conductivity of the film using two probe DC measurements.

Figure 4 shows the temperature dependence of the conductivity of the YSZ films on sapphire. The conductivity of the porous film with powder and polymer ratio of 5:1 is about one order of magnitude lower than that for dense sample (with the ratio 1:1). The conductivity of this porous film produced at 400˚C at heat up is higher than the conductivity after heating to 900˚C. This is probably related with the densification of nanocrystalline YSZ derived from the polymer, which causes a decrease in the contact area between grains in this porous material. In contrast, the conductivity of the dense film produced at 400˚C is lower than the conductivity after heating to 900˚C, which can be explained by the crystallization of polymer derived YSZ. In this case the material is dense and the contact surface area can not be changed, so crystallization will cause only a decrease of the grain boundary volume. It is known that a decrease of the grain boundary volume results in an increase of the total conductivity of the film [8]. The final conductivity (after short time annealing at 900^{o}C) for both specimens is stable and does not change after the subsequent annealing at 900^{o}C. The conductivity and activation energy for the dense film are very close to those reported for bulk YSZ [9].

The measurements on platinum foil substrate were made using in the thickness configuration (Figure 5a). In this case more information can be obtained from the impedance spectra, because the grain and grain boundary capacitances are higher than that of the sample holder capacitance, so grain and grain boundary resistances can be separated. In this measurement electrode resistance can not be neglected and should be taken into account. Moreover the platinum substrate acts as a blocking electrode for oxygen ions, so low frequency resistance should be very high and should contain information about the electronic leakage of the film. Figure 5b shows an equivalent circuit, which is appropriate in this measurement. The elements of the equivalent circuit are represented by the resistance R_g and capacitance C_g of grain, resistance R_{gb} and capacitance C_{gb} of grain boundary and resistance R_{leak} and capacitance C_{leak} connected with the blocking effect of the platinum electrode.

Figures 5c and 5d show typical impedance spectra obtained for YSZ film on a platinum substrate. In the temperature range from 200°C to 400°C the spectra consist of 2 closed semicircle (grain semicircle in the high frequency range and grain boundary semicircle in the middle frequency range) and an open semicircle in the low frequency range connected with leakage of the film

(Figure 5c). When the temperature increases, the impedance spectra shift to higher frequencies. The grain semicircle shifts out of the measurements range (f>1MHz) and at 300^{o}C starts to disappear. The grain boundary semicircle shifts out of the measurement range at 450°C. At the same time the leakage semicircle shifts in the measurement range and starts to be fully visible at temperatures above 450°C (Figure 5d). The impedance spectra were fitted to the equivalent circuit presented in Figure 5b. When necessary the circuit was appropriately corrected, e.g. once the semicircle disappears from the spectra, suitable capacitance was removed from the equivalent circuit.

The temperature dependences of the grain, grain boundary and leakage conductivities were calculated and are presented in Figure 6. Below 450°C, grain and grain boundary conductivity were plotted individually, while above 450°C the grain and grain boundary conductivity could not be separated so only the total ionic conductivity is presented. Both, the activation energies and the values of grain and grain boundary conductivities are in good agreement with the literature data for bulk YSZ [9] and with that measured in plane on the sapphire substrate. So it is possible to conclude that net shape technology allows the preparation of YSZ films with high ionic conductivity at the temperatures as low as 400^{o}C on both sapphire and platinum substrates. The conductivity related to the blocking effect of the platinum electrode is included in the Figure 6 as well. As it was previously mentioned the platinum acts as a blocking electrode for oxygen ions, because the oxygen can not penetrate dense platinum foil. If an ideal blocking effect occurs vertical line on the impedance spectra should be visible in the low frequency range [10]. Any sources of the leakage through the film will change this phenomenon (non ideal blocking). The non ideal blocking could be related to different physical effects like (i) ionic edge leakage, (ii) gas leakage of the film and (iii) hole/electron leakage. The effects are schematically presented in a Figure 7 and described below.

(i) A bottom platinum electrode is sealed by the film under the top contact, but it is open to the surrounding air at the edges of the substrate, so ionic conductivity between the edges of the substrate and the top electrode should be taken into account. This ionic leakage is not connected with the quality of the material but only with the geometry of the sample and it should be very small because of particular geometry of the sample. In our case the ratio between the ionic conductivity through the film and ionic edge leakage should be at least a factor of 10^{6}. As can be seen, the experimental value of the leakage is much lower. In addition, the activation energy of about 1eV should be expected because the leakage is of ionic character, whereas the experimentally observable activation energy is much higher (2.2eV). So it is possible to conclude that the leakage of the film is not connected with ionic edge leakage.

(ii) If a film has open porosity (gas leakage through the film), the molecular oxygen can penetrate through the film. The gas leakage is an important feature of the electrolyte materials, which influences the performance of variety of devices. Net shape processed YSZ appears to be dense from the microstructural investigation, but it can have some open porosity visible only in electrical measurements. The activation energy of the leakage conductivity should be very low, if we dealing with gas leakage [11]. The experimental value of the activation energy is high (2.2eV) and does not fit to gas diffusion. It is possible to conclude that net shape processed YSZ does not have

open porosity, or at least this porosity is so low that it can not influence the electrical properties of the electrolyte.

(iii) It is known that YSZ in air is a p-type conductor and exhibits hole conductivity, which is several orders of magnitude less than the ionic conductivity. This conductivity will cause the leakage in the sealed structure (electronic leakage). Several authors have measured hole conductivity of the bulk YSZ using different methods [12-20]. The observed values of the hole conductivity and activation energy are widely scattering (E_h differs from 1.5 to 2.4eV), however values are in reasonable agreement with calculated the activation energy (2.2eV) of the leakage conductivity.

Based on the presented analysis it can be concluded that electrical leakage of the film observed on the impedance plots is not connected with open porosity of the film, but most likely with the hole conductivity of YSZ. This is an important feature for these YSZ films, since it confirms that dense, high quality YSZ 1-10 μm thick films can be prepared at temperatures as low as 400˚C.

SUMMARY

The possibility to use net shape technology for deposition of YSZ film of the thicknesses from 1 to 10 μm on dense substrates was investigated. YSZ films were deposited by the net shape process on sapphire and platinum foil and characterized. It was shown by a microstructural investigation that dense YSZ coatings can be obtained at temperatures as low as 400^{o}C. Electrical measurements show that grain and grain boundary conductivities of net shape processed YSZ are comparable with those observed for high temperature sintered bulk ceramic. The electrical leakage of net shape processed YSZ is low and is not connected with open porosity of the film, but most likely with the hole conductivity of YSZ.

Acknowledgments

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Figure captions

Figure 1. SEM images of the cross-section of a fracture cross section of 3 μm thick YSZ film on sapphire: a. powder and polymer ratio of 1:1 sintered at 400˚C; b. powder and polymer ratio of 1:1 sintered at 900˚C; c. powder and polymer ratio of 5:1 sintered at 900˚C

Figure 2. SEM image of the cross-section (a.) and AFM image of the surface (b.) of 1 μm thick YSZ film on Pt foil.

Figure 3. Schematic diagram of in plane measurement of YSZ film on sapphire (a), the equivalent circuit (b) and typical impedance spectra at 800˚C (c).

Figure 4. Temperature dependence of conductivity of YSZ film on sapphire.

Figure 5. Schematic diagram of measurement configuration though YSZ film on platinum (a), the equivalent circuit (b), typical impedance spectra at 300°C (c) and at 700°C (d).

Figure 6. Temperature dependence of conductivity of YSZ film on Pt foil.

Figure 7. Schematic representation of source of non-ideal blocking electrode effect of platinum support.

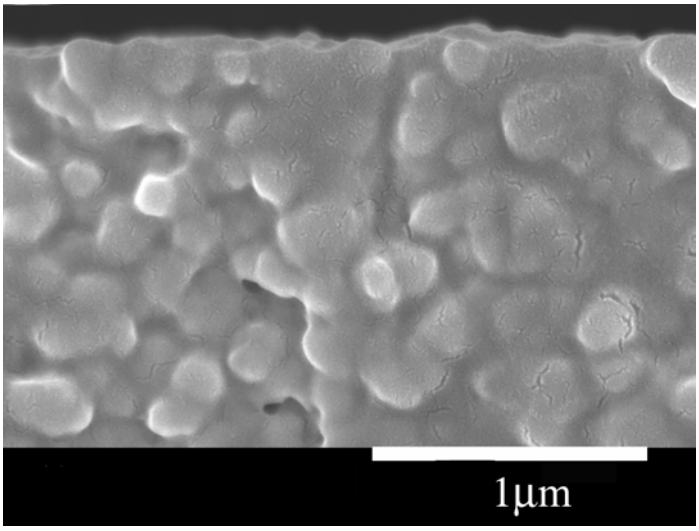
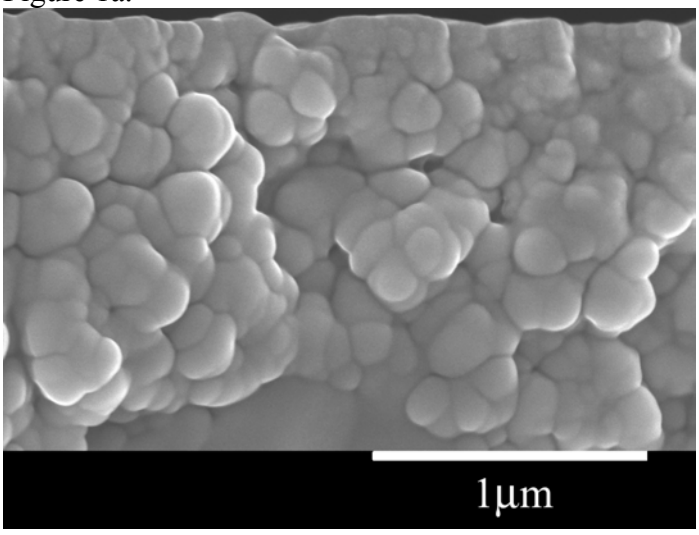


Figure 1a.



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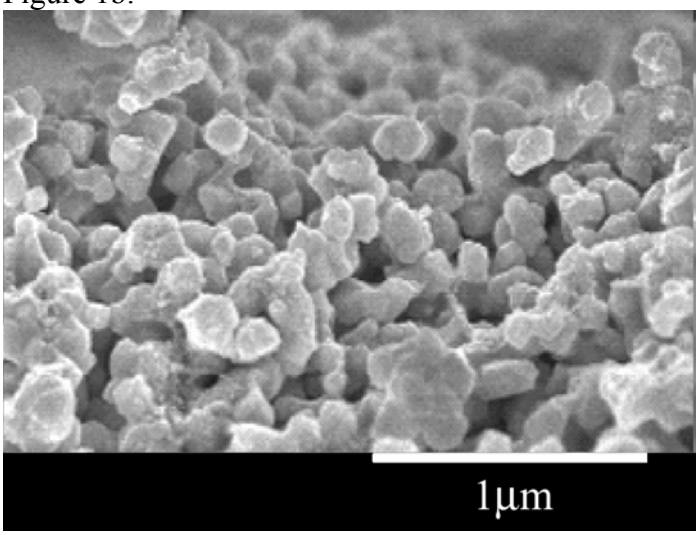

Figure 1c.

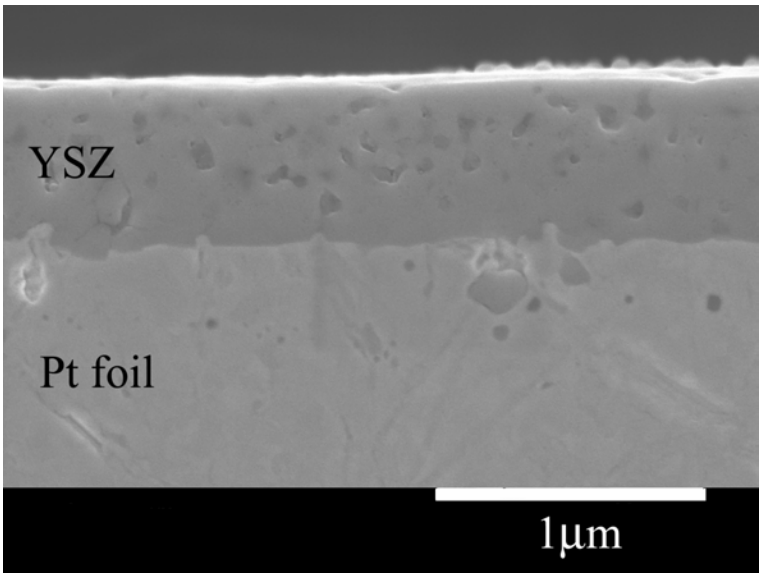

Figure 2a.

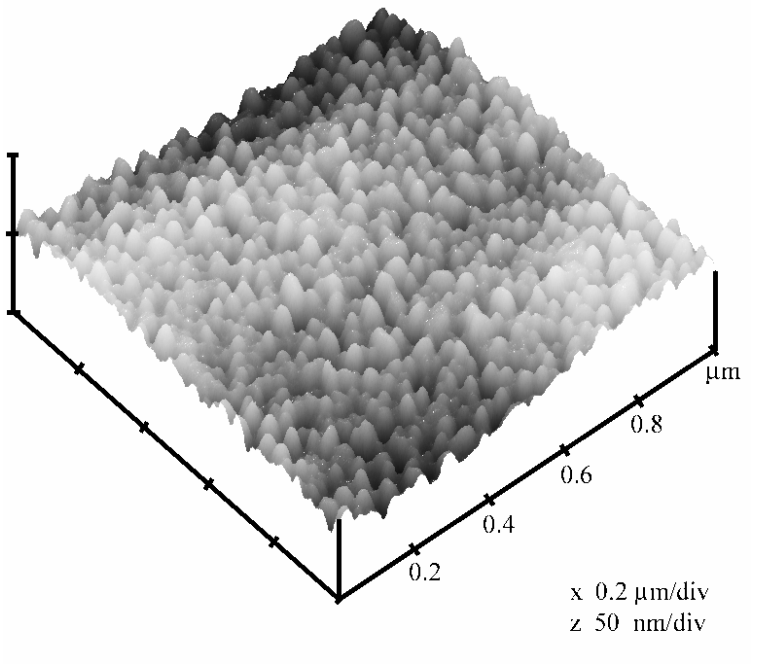

Figure 2b.

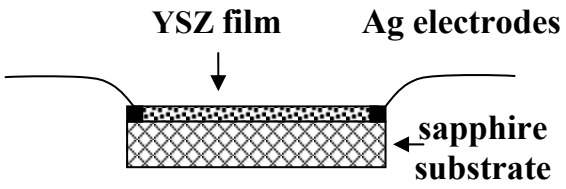

Figure 3a.

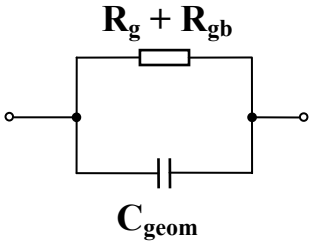

Figure 3b.

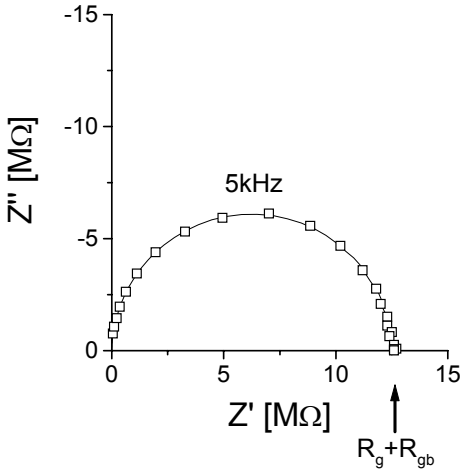

Figure 3c.

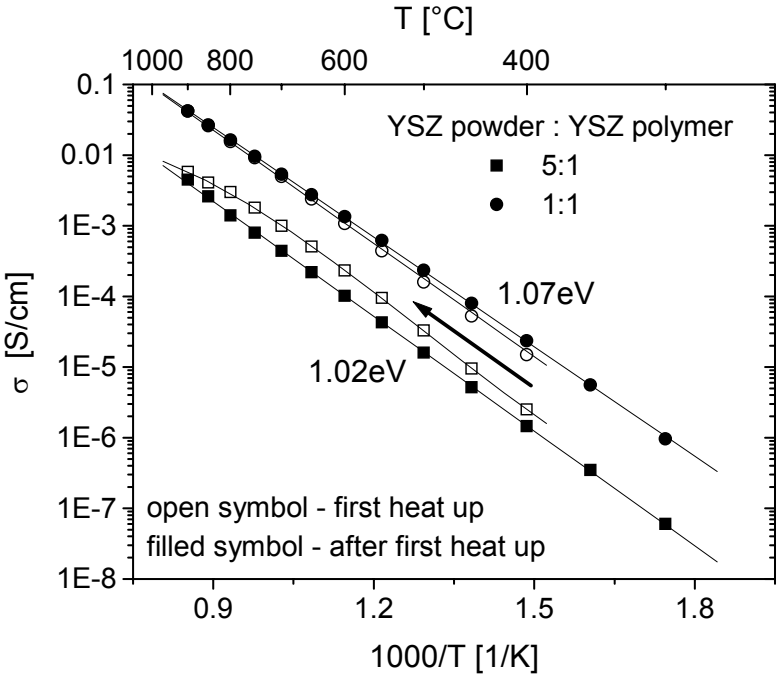

Figure 4.

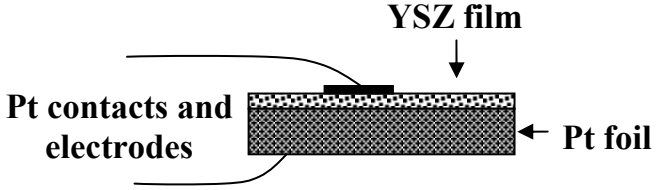

Figure 5a.

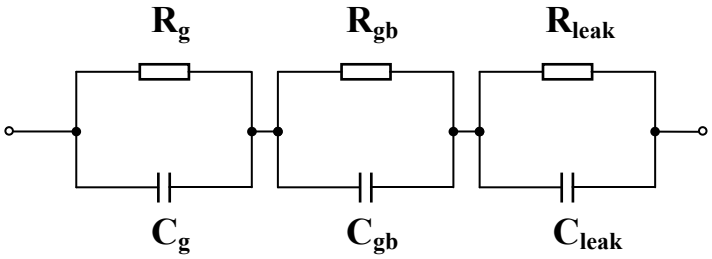

Figure 5b.

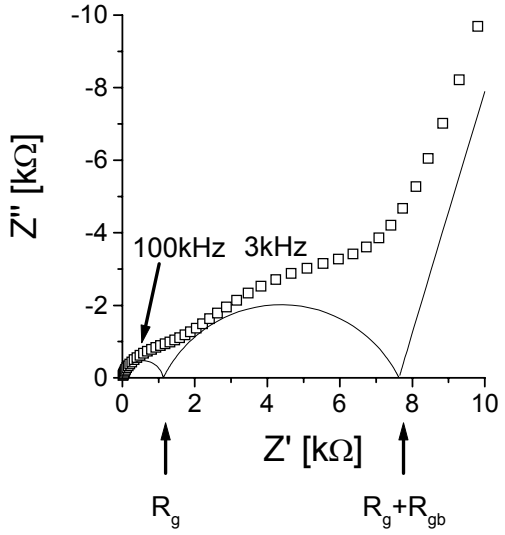

Figure 5c.

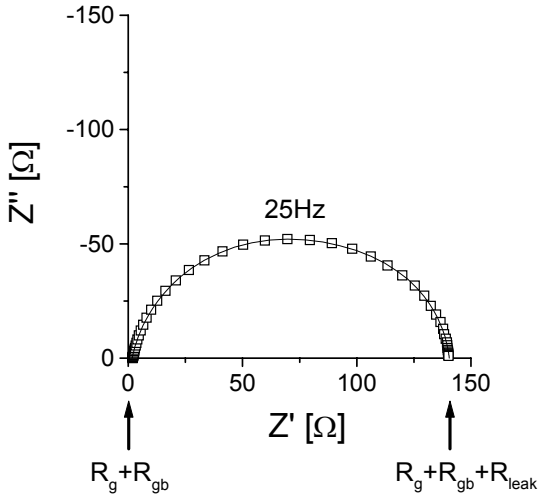

Figure 5d.

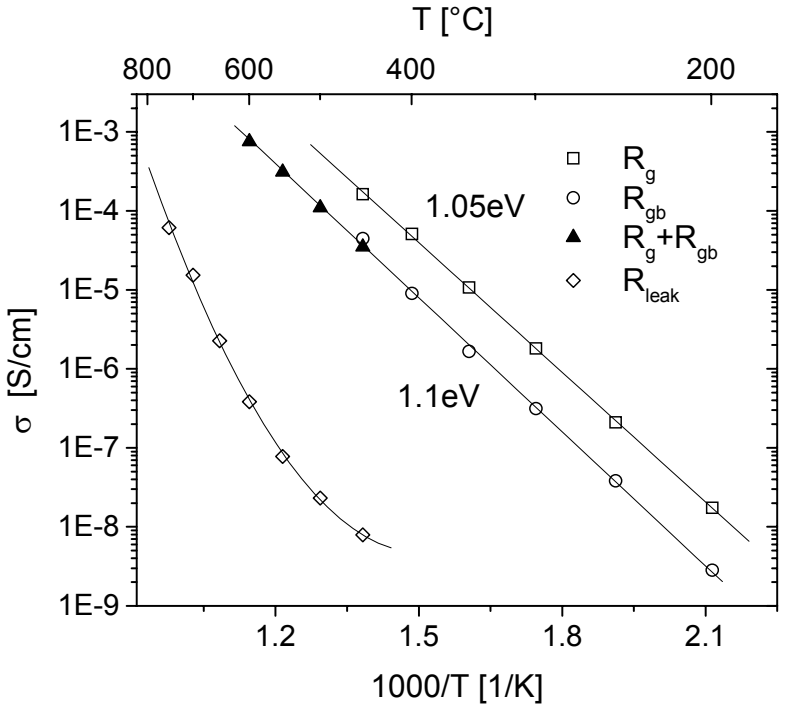

Figure 6.

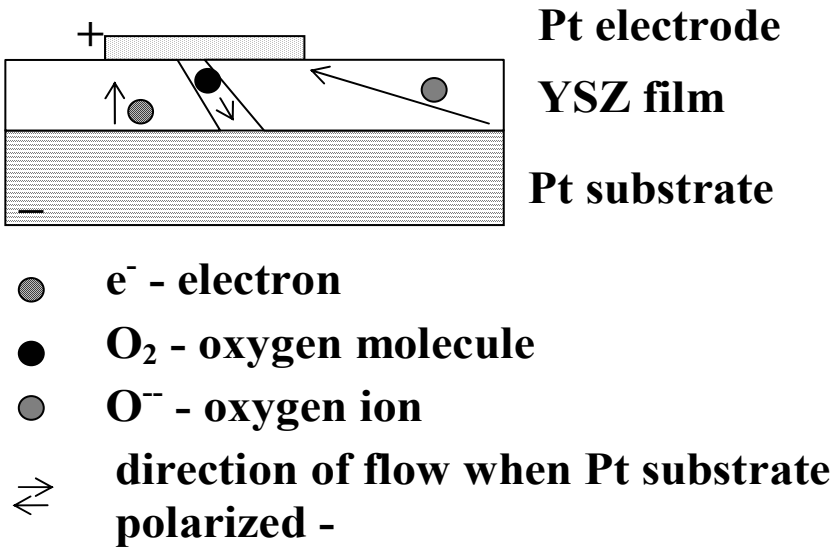

Figure 7.

Appendix C-1

Low Temperature Processing of Thin Film Electrolyte for Electrochemical Devices

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ABSTRACT

Thin film electrolyte processing has become a key issue for the development of electrochemical devices. In this study, yttrium stabilized zirconia (YSZ) thin film with thickness of 1-2 μm electrolyte has been prepared on dense and porous substrates using a combination of colloidal suspensions and polymer precursors at annealing temperatures < 1000°C. Use of processing temperatures < 1000°C minimizes interfacial reactions between electrolyte and anode/cathode materials. The conductivity of the thin film annealed at 900°C was measured and found to be the same as that of bulk YSZ and the processing temperature to obtain such conductivity was as low as 400°C.

Solid oxide fuel cells (SOFCs) are considered as being one of the important future energy sources [1]. Before these cells can become widely utilized, there are several problems that need to be solved. Among them are the interfacial reactions which occur between the anode/cathode and electrolyte which occur due to high temperature processing cause losses in the cell and limit performance of cell. There have been a number of reports which suggest that the solution to this problem if to introduce an interlayer to prevent the interfacial reaction [2]. On the other hand, this note offers perhaps a simpler solution, which is to decrease the processing temperature of the cell.

A low temperature thin film processing method (under 1000°C) for preparing dense, nanocrystalline electrolyte materials such as doped ZrO_2 and CeO_2 has been reported which uses the polymer precursor spin coating technique [3, 4]. The thickness of these films is <1 micron so the resistance of the electrolyte is low, thereby enhanceing the cell performance [5]. Because of these facts, low temperature thin film electrolyte processing has become a key issue for the development of SOFC. However, to apply the polymer precursor spin coating technique to SOFCs, there are several problems such as the difficulty for obtaining thick film above 1μm and limitation of application to only dense substrates. In this study, a combination of colloidal suspensions and polymer precursors has been used to prepare coatings on both porous and dense substrates which yield 1-2 μm thick dense films of yttrium stabilized zirconia (YSZ) film after annealing at temperatures < 1000°C.

The dense YSZ films were prepared by coating the surface of both dense sapphire and (La, Sr)MnO_3 porous substrates with a colloidal suspension which contained YSZ particles (size ~ 100 nm). After which, a polymer precursor solution which produces YSZ upon heating, impregnated the colloidal coating. (The process is illustrated in Fig. 1). After drying, the composite coating is heated to temperatures < 400°C to convert the polymer phase to YSZ. A dense film can be obtained after a series of applications of the polymer precursor (the number of applications depends upon the solids content of the polymer precursor and the porosity of the colloidal film.) For the preparation of the YSZ polymer precursor, the details were discussed elsewhere [6]. Details of the preparation of the composite are withheld, due to a patent application.

Figure 2 shows SEM images (Hitachi S4700) of a YSZ film on a sapphire substrate for different annealing temperatures (400 and 950^{o}C). As can be seen, the film thickness is around 1.5 μm, and YSZ particles are surrounded by a nanocrystalline continuous dense YSZ layer introduced by the polymer precursor. After annealing at 900^{o}C, it is observed that the densification of continues in the YSZ layer and a dense nanocrystalline grain structure (100 ~ 200 nm) develops. One of advantages of the colloidal-polymer method is shown in Fig. 3. Figure 3 shows SEM images of a YSZ film on a porous substrate (annealing temperature = 900^{o}C). This is a continuous defect-free dense YSZ layer of thickness ~ 2 μm. The thickness of the film can be easily controlled from 0.5 – 20 μm by changing the YSZ concentration in the YSZ colloidal suspension.

The electrical conductivity of the resulting YSZ films was studied using a Solartron 1260 frequency response analyzer with a 1296 Interface. Silver paste was used as electrodes and measurements were conducted in air over the temperature range from 400 to 800^{o}C. The electrical conductivity of YSZ film (annealed 900 ^{o}C) were calculated and shown in Fig. 4 as a function of temperature along with the values from the literature [7]. As can be seen, the conductivity of the films are close to that reported for bulk YSZ, which shows the quality of the film prepared at low temperature. From these results, the area specific resistance of this YSZ thin film with 1.5μm thickness can be estimated and found to be 0.11 Ωcm^2 at 600^{o}C, 0.6 Ωcm^2 at 500^{o}C. Figure 5 compares the electrical conductivity of YSZ film prepared at 400^{o}C by this technique to that using the polymer precursor process by itself [6] and dense YSZ prepared by the conventional tape cast technique, as a function of annealing temperature. For the tape cast technique, the same YSZ powder was used as that used to prepare the colloidal suspension. As can be seen, the annealing temperature needed to obtain the conductivity observed for dense YSZ depends upon the processing techniques with that required for colloidal-polymer method being the lowest at 400^{o}C. Application of the colloidal-polymer method to other electrochemical devices can be expected to bring significant improvement of their performances.

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Figure Captions

Figure 1: The schematic diagram of colloidal -polymer process.

Figure 2: SEM images of YSZ thin film on dense sapphire substrate annealed at (a) 400^{o}C (b) 900^{o}C.

Figure 3: SEM images of YSZ thin film on porous substrate annealed at 900^{o}C (a) cross section (b) surface.

Figure 4: The electrical conductivity of the YSZ thin film on dense sapphire substrate annealed at 900^{o}C.

Figure 5: The electrical conductivity of the YSZ thin film as a function of annealing temperature along with results from several processing techniques.

Fig.1

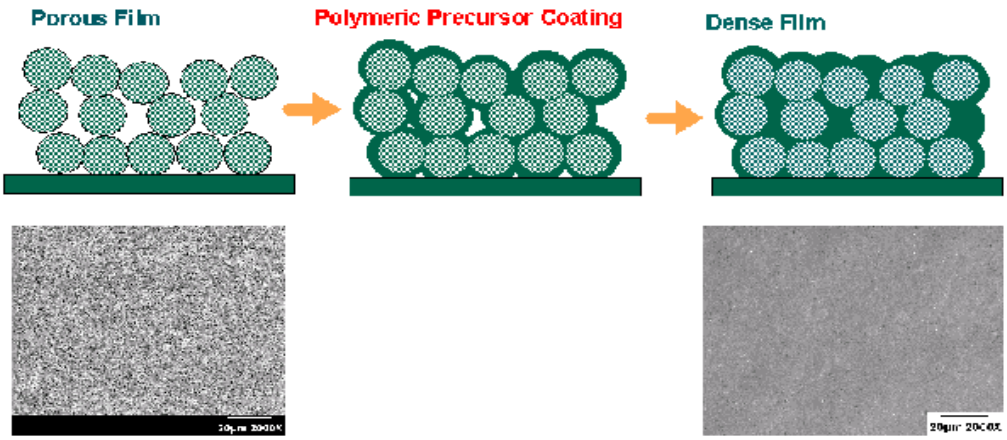

Porous Film
Polymeric Precursor Coating
Dense Film

Fig.2

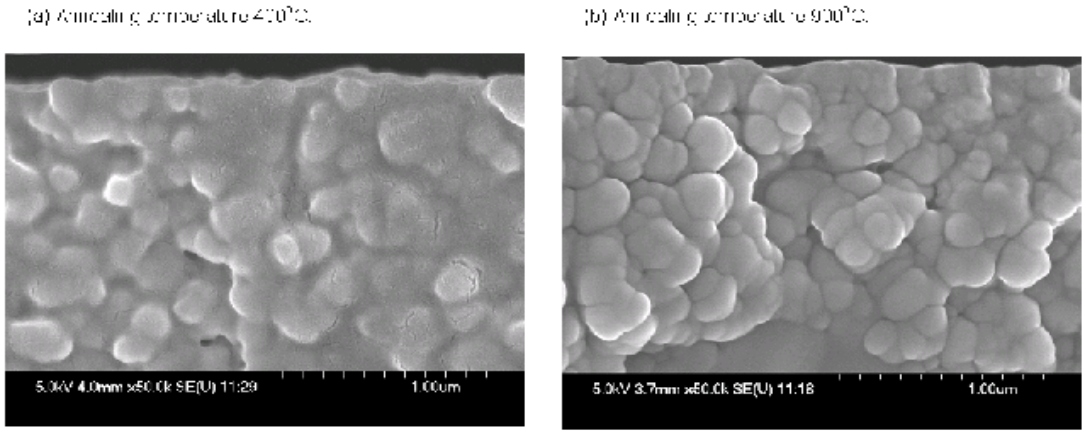
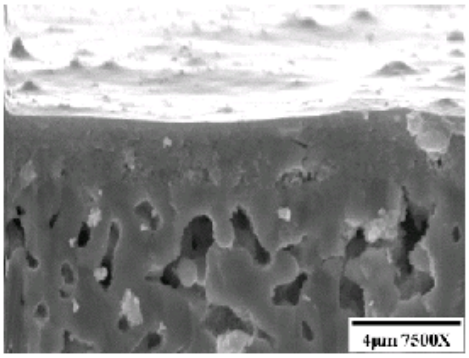

(a) Annealing temperature 400°C.
(b) Annealing temperature 900°C.
5.0kV 4.0mm x50.0k SE(U) 11:29
1.00um
5.0kV 3.7mm x50.0k SE(U) 11.18
1.00um

Fig 3

(a) Cross section



(b) Surface

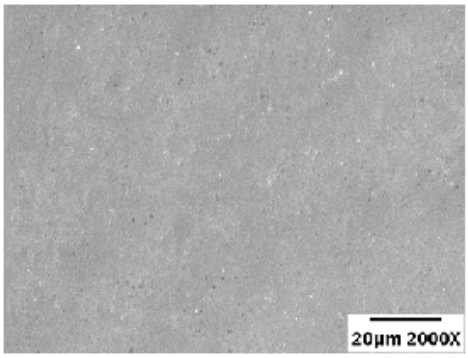
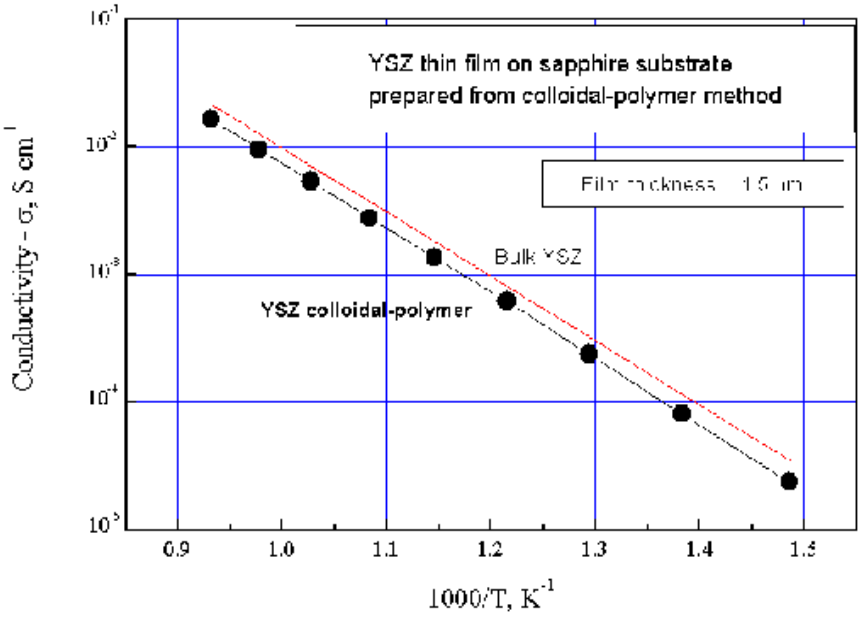
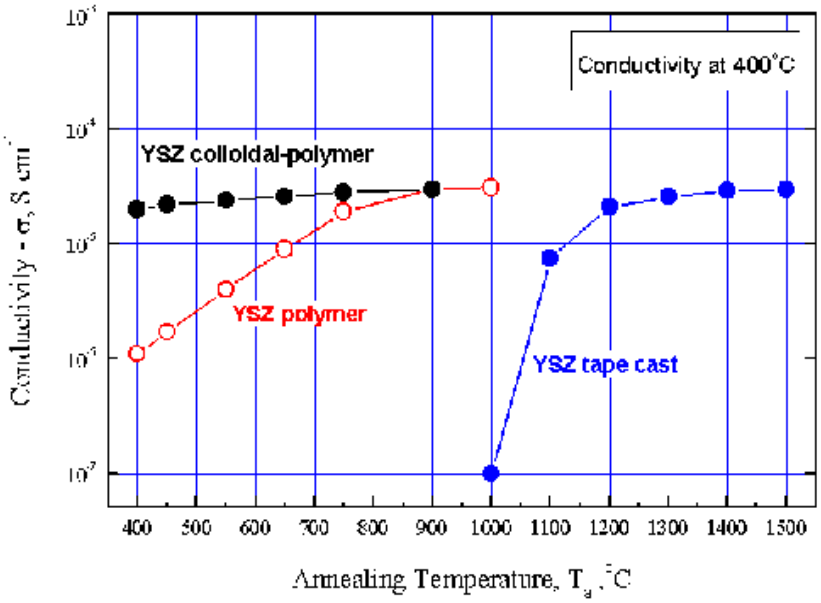


Fig 4




Conductivity at 400°C
YSZ colloidal-polymer
YSZ polymer
YSZ tape cast
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
Annealing Temperature, T_a, °C

Appendix C-2

Application of Composite Technology for SOFCs

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Application of Composite Technology for SOFCs

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ABSTRACT

Composite technology is a new approach to solid oxide fuel cell (SOFC) fabrication. It is based on the net shape processing, which uses a combination of colloidal suspension and polymer precursor techniques. Different elements of SOFC can be prepared and optimized using this approach and the flexibility of the net shape processing. The goal of this research was to develop net shape procedures for different elements of SOFC, to show the real possibility preparing all these elements of SOFC and to investigate the advantages of composite technology. A nickel-YSZ composite was prepared and investigated as the prospective anode material. High electronic conductivity and stability in REDOX cycles were shown for this material. Different cathode compositions were prepared using composite technology and tested. It was shown, that these materials ensure low overpotentials and are time stable at operation temperature up to 800^{o}C. All three SOFC designs were tested: anode, cathode and electrolyte supported SOFCs. It was possible to achieve low resistance of SOFC structure for all designs, but electrode supported SOFCs had limitation in the current connected with the gas diffusion through thick electrode substrates. The best performance was achieved on an electrolyte supported system with 100 μm YSZ electrolyte and composite anode and cathode: 0.75W/cm^2 power density at 0.6 V at 800^{o}C.

INTRODUCTION

Solid oxide fuel cells (SOFCs) are one of the most important perspective energy conversion devices [1]. The main demand in the current SOFC development is lowering the operation temperature to the range of 600˚C – 800˚C. It is necessary to decrease the resistance of the electrolyte and both electrodes (cathode and anode overpotentials) in order to lower operational temperature and to increase or at least sustain performance in comparison with high temperature SOFCs.

One of the ways to lower operation temperature is to decrease the thickness of the electrolyte. That is the reason why electrode supported systems is the design of choice for the most of the developers. It is not possible to deposit dense electrolyte on pre-sintered substrate (anode or cathode) by powder based technologies, so high temperature co-sintering is technology of choice [2-4].

Yttria stabilized zirconia (YSZ) is the most commonly used material as the SOFC electrolyte and several approaches have been made to develop thin film YSZ deposition techniques on either the anode or cathode. The methods include chemical and physical deposition, such as Electrochemical Vapor Deposition (EVD) [5] or magnetron sputtering [6], and liquid precursor and powder processing techniques such as polymer spin coating [7] or tape casting [8]. The detailed description of YSZ thin film fabrication techniques can be found in the review article [9]. All these techniques experience difficulties with deposition of 1 to 10 μm

electrolyte layers. Powder based techniques (such as tape casting, laminating, screen printing, etc.) require high temperature co-sintering of the electrode and electrolyte. This limits application of these techniques to anode supported SOFCs because of chemical reactions between cathode and electrolyte during the sintering process (in cathode supported design). In contrast to powder based techniques, polymer based techniques limit the thickness to ~100 nm per deposition because of the shrinkage connected with organic decomposition and 1 μm seems to be the upper limit for this approach even for multiple depositions. In general, chemical and physical deposition techniques allow deposition of dense YSZ layers at low temperature, but the cost of this kind of processing is too high for widespread.

The intent of this research was to develop a low temperature method for deposition of 1 to 10 μm thickYSZ electrolyte using combination of YSZ powder and YSZ polymeric precursor (net shape processing). In this process the powder is first deposited onto the surface to provide a framework of connected grains into which the polymeric precursor impregnates to form an oxide particle / organic polymer film. Upon heating to 300^{o}C, the polymer decomposes to yield a nanocrystalline layer of YSZ, which fills the space between the grains, so dense material can be prepared without shrinkage during further annealing. One of the goals of this research was to show the possibility to deposit dense electrolyte layers at low temperature using net shape processing, to investigate structural stability of these layers at elevated annealing temperatures and to compare electrical properties with those for YSZ electrolytes prepared by commonly used techniques (high temperature sintered bulk ceramics).

Low electrode overpotentials are required for the low temperature SOFC applications [10]. Composite technology allows to create the electrodes with higher effective surface area, to increase efficiency of the exchange reactions, and, consequently, to decrease electrode overpotentials [11-14]. Net shape processing has a potential for electrode material optimization, because of lower processing temperatures and better control of the composition (in comparison with powder based technologies).

This investigation would be not completed without testing of three-layer SOFC structures. Different three-layer structures were prepared using net shape processing: anode, cathode and electrolyte supported. Impedance spectroscopy and direct SOFC measurements were used to characterize these structures.

EXPERIMENTAL

Nanocrystalline powders with the grain size 50 to 100 nm and metal organic polymeric precursors prepared by the technology described elsewhere [7,12] were used for the preparation of all composite materials investigated..

Scanning Electron Microscopy (SEM) images were obtained using Field Emission Scanning Electron Microscope Hitachi S-4700 and Battery Tester Solartron 1470 together with Impedance Gain Phase Analyzer Solartron 1255 was used for impedance measurements and SOFC performance testing.

Dense YSZ coatings were successfully prepared on different substrates including dense (sapphire, platinum foil) and porous (YSZ-Ni anode and LSM cathode). It was shown that the thickness range 1 to 10 μm can be overlapped by net shape processing, and, what is important, the preparation temperature for the dense YSZ electrolyte can be decreased to 400^{o}C. SEM images of the structure cross-sections for ~2 μm coatings on LSM substrate are shown in Fig.1

as an example. These coatings were initially prepared at 400°C and than annealed at 900°C to ensure stability of the YSZ layers at elevated temperatures. It can be seen from the figure, that net shape processing allows the preparation of dense coatings on porous substrates and exhibits good planarization properties: it is possible to prepare smooth, defect free coating with the thickness less than 2 μm on porous substrates which have pore size of several microns. The electrical properties of the coatings are close to the properties obtained with high temperature sintered ceramic materials and are stable with the further high temperature annealing (Fig.2): up triangles in Fig.2a shows Ahrrenius plot for as-prepared (un-annealed sample) and down triangles refer to the sample annealed at 900°C. Fig.2b illustrates the fact that net shape processing can yield the same value of conductivity of composite YSZ with the annealing temperature below 600°C as dense ceramic YSZ sintered above 1200°C.

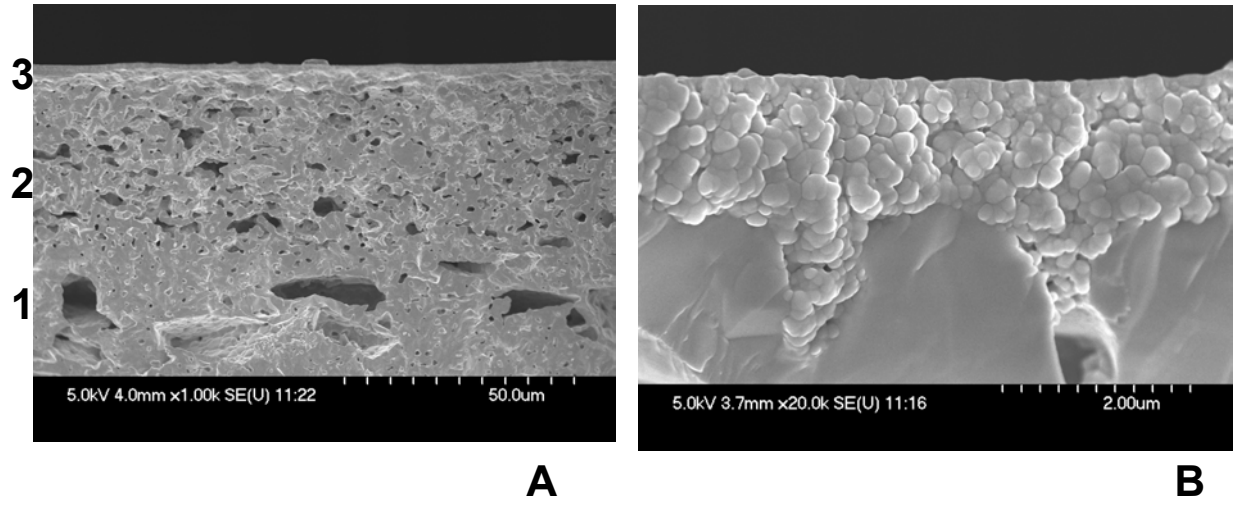

Fig.1. SEM images of the cross-sections for dense composite YSZ films on porous LSM substrates.
A – Low magnification;
B – High magnification.

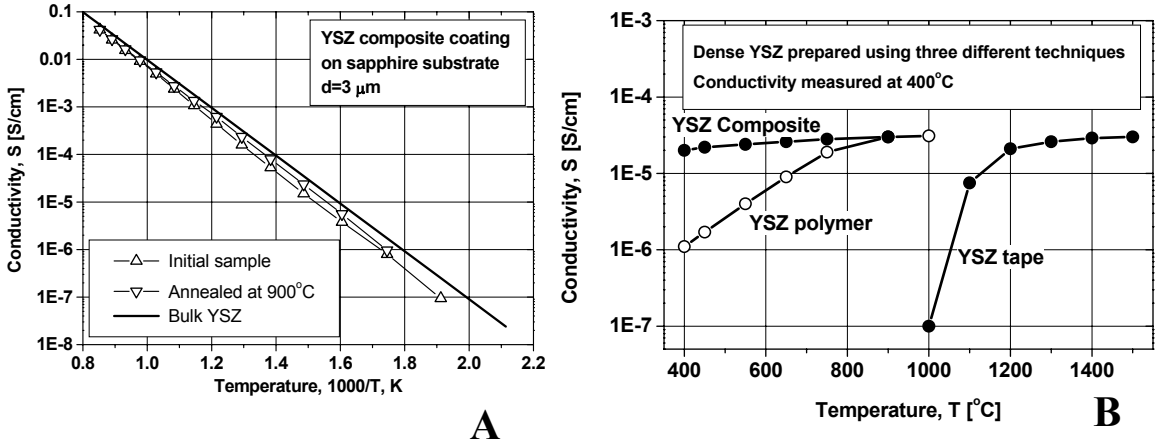

Fig.2. Electrical properties of composite YSZ coatings.
A – Temperature dependence of the conductivity for composite YSZ;
B - Conductivity of YSZ prepared by different techniques as a function of sintering temperature.

Ni-YSZ composite coatings were prepared on different substrates to investigate an applicability of the net shape processing for SOFC anodes. Fig.3 shows the results obtained for composite coatings on sapphire substrate. It can be seen from Fig.3a that the conductivity of YSZ/NiO composite in air is higher than that of YSZ by itself. Upon reduction Ni conductivity increased to ~500 S/cm. It is important that composite Ni-YSZ cermet shows stability as it undergoes REDOX cycles, which is illustrated in Fig.3b.

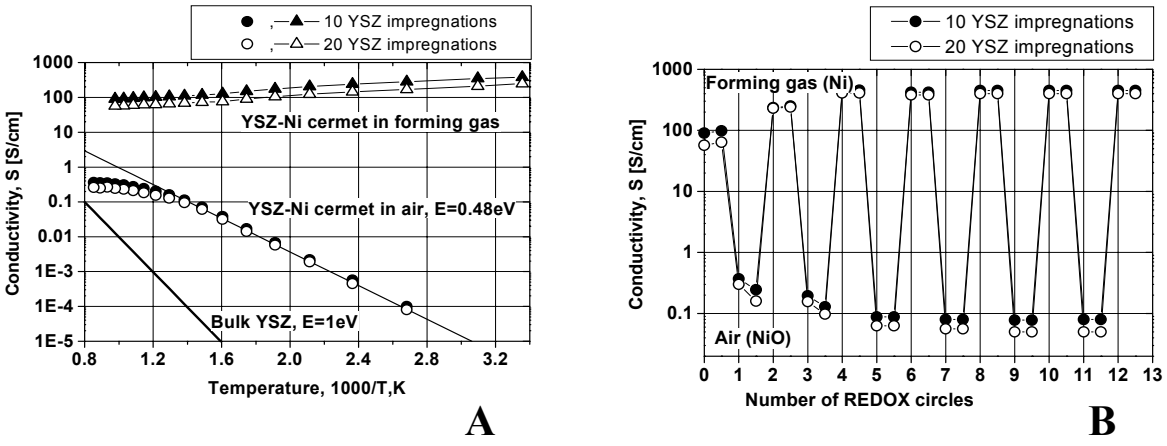

Fig.3. Electrical properties of net shape processed YSZ-Ni composite.
A – Temperature dependence of the conductivity in air (NiO phase) and in forming gas (Ni phase);
B – REDOX stability of composite Ni-YSZ cermet.

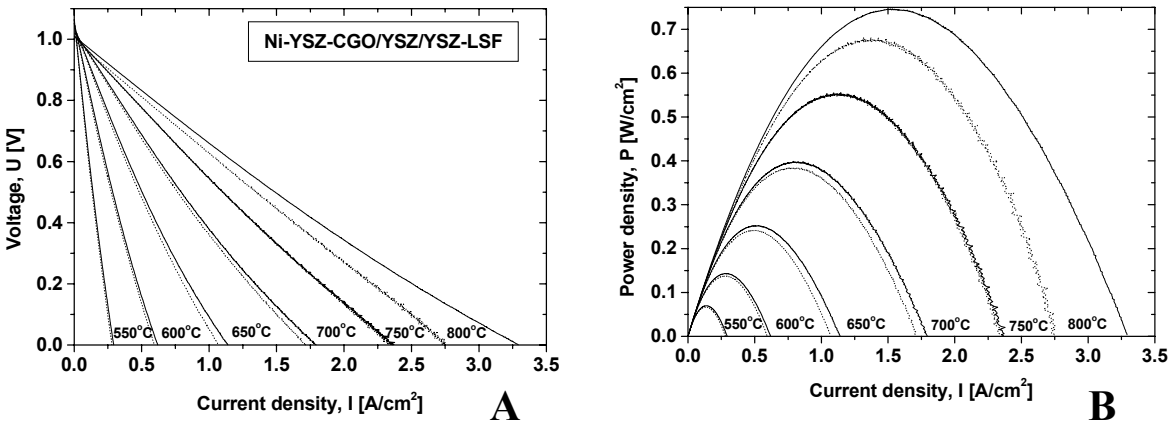

Fig.4. SOFC testing results. Electrolyte supported design with 100 μm YSZ electrolyte, Ni-YSZ-CGO composite anode and YSZ-LSF composite cathode.
A – Current to voltage characteristics in the temperature range 550 to 800°C;
B – Power density in the same temperature range.

Different composite cathodes were also prepared and tested including LSM-YSZ, LSF-YSZ, LSCF-YSZ and SSC-YSZ compositions. It was shown by investigation of the symmetrical structures cathode-electrolyte-cathode that these cathodes have low resistance (on the level of 0.05 Ohm.cm^2 at 800^{o}C) and show resistance towards degradation.

Fuel cell testing was accomplished on anode, cathode and electrolyte supported SOFC structures with all elements prepared using net shape processing. It was shown that overall resistance of SOFC structures is low (on the level of 0.25 to 0.3 Ohm.cm^2 at 800^{o}C), but gas diffusion through the substrate did limit maximum current density on electrode supported samples. The best results were achieved on electrolyte supported SOFCs with 100 μm YSZ electrolyte (Fig.4). It can be seen that I-V characteristics are almost linear and power density is on the level of 0.75 W/cm^2 at 800^{o}C. REDOX cycles were provided at each temperature investigated (see dotted and solid lines in Fig.4). It can be seen that composite SOFCs are stable in REDOX cycles up to ~750^{o}C.

SUMMARY

The possibility of using net shape technology for preparation of the trilayer (anode/electrolyte/cathode) elements of a SOFC was shown. The features of net shape processing (possibility to prepare and to densify the material at very low temperature and precise control of the composition) allow deposition of dense electrolytes (thickness range 1 to 10 μm) on pre-sintered substrates and efficient electrodes (anode and cathode). Net shape processing opens additional ways for optimization of SOFC elements and could be helpful for different designs of the SOFC.

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