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Electrical Properties of YSZ Films Prepared by Net Shape Technology

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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°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 temperatures as low as 400°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.
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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 600-800°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 1-10 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 cosintering 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 processing is too high for widespread applications.

The aim of this research was to develop a low-temperature method for deposition of 1-10 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 film. Subsequent and multiple depositions of polymer precursor fill the space between the particles, providing dense YSZ structure. Therefore dense materials can be prepared without shrinkage even during further annealing, because the densification process is mainly limited to the growing of YSZ nanocrystallites derived from polymer precursor on YSZ powder. In other words, YSZ powder is used to prepare net-shape green body, while the YSZ polymer densifies it. 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 100 nm, which was dispersed ultrasonically in water and ethanol. The suspension contained about 50 wt % YSZ powder. The YSZ polymer was prepared using zirconium chloride and yttrium nitrate precursors (Alfa Aesar). Our previous studies of YSZ films derived from polymer precursor only shows that single-phase single YSZ structure is obtained at as low as 400°C.[8] A schematic diagram of film preparation is presented in Fig. 1. First a few depositions of colloidal suspension and then several depositions of polymer precursor are spin-coated on the substrate. The thickness of the film is mainly controlled by the number of colloidal suspension depositions, while the ratio between YSZ powder and YSZ derived from polymer precursor controls the final porosity of the material. For the present concentration of the suspension and with the spin speed of 1000 rpm, the thickness of about 1 μm per one deposition of colloidal suspension was obtained. Dense material can be prepared if the ratio between YSZ powder and polymer precursor is equal to 1:1. The materials with controlled porosity can also be 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 1-3 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 6517A electrometer. The dc results were confirmed by two-probe impedance spectroscopy, which was performed using a Solartron 1296 dielectric interface together with a Solartron 1260 impedance

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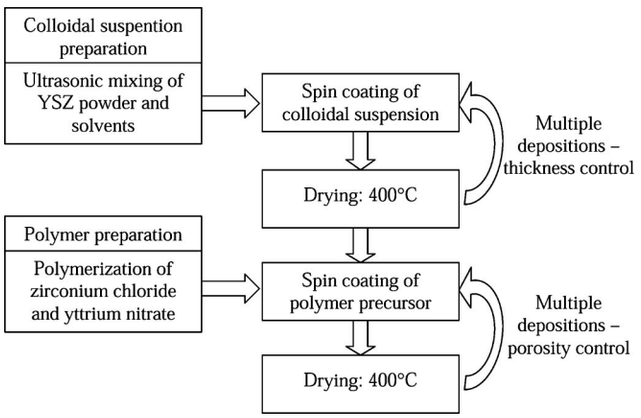

Figure 1. Schematic diagram of film preparation by net shape technology.

gain phase analyzer (in-plane measurements). The measurements through the film were performed using a Solartron 1470 battery tester and Solartron 1255 impedance gain phase analyzer. All measurements were carried in air.

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 preannealed at 800°C for 2 h and reannealed 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 Fig. 2 and 3. The images of the cross sections for the films on the sapphire are presented in Fig. 2. Figure 2a 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 (Fig. 2b) the crystallization process is completed and only 100-200 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 (Fig. 2c). This type of material cannot be used as an 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 3 shows an 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-sectional SEM image (Fig. 3a) 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

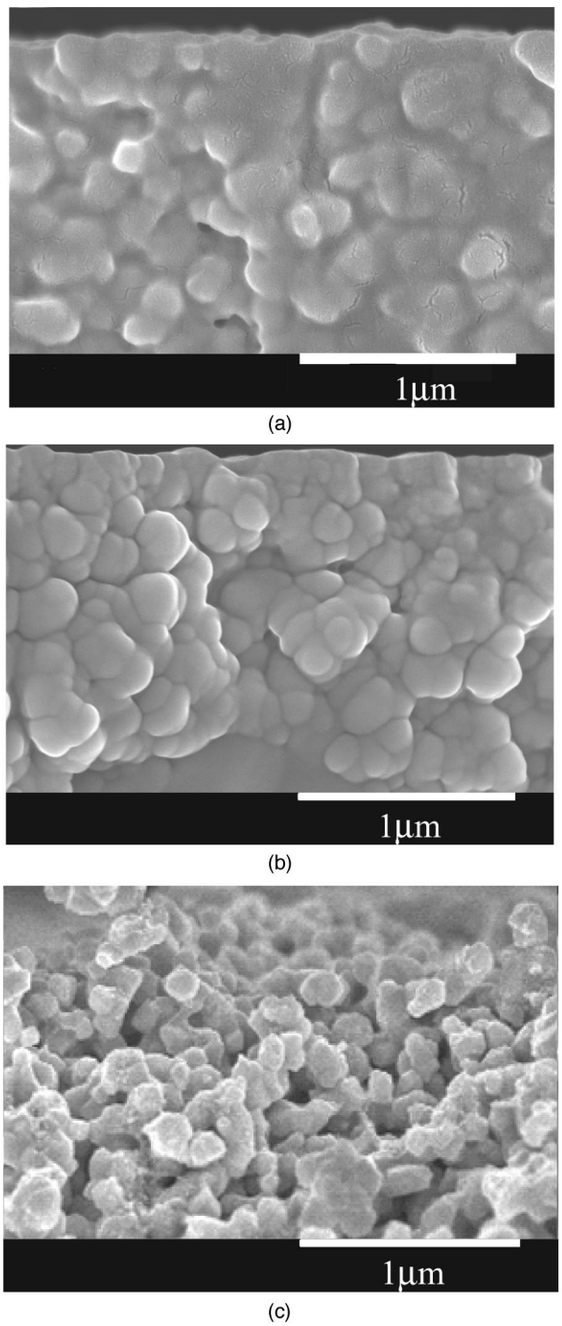

Figure 2. SEM images of the cross section of a fracture cross section of 3 μm thick YSZ film on sapphire: (a, top) powder and polymer ratio 1:1 sintered at 400°C; (b, middle) powder and polymer ratio 1:1 sintered at 900°C; and (c, bottom) powder and polymer ratio 5:1 sintered at 900°C.

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 (Fig. 3b). The value of this grain size estimated from the AFM image is 50 nm 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 the same as those of bulk YSZ ceramic material? In order to answer this question the

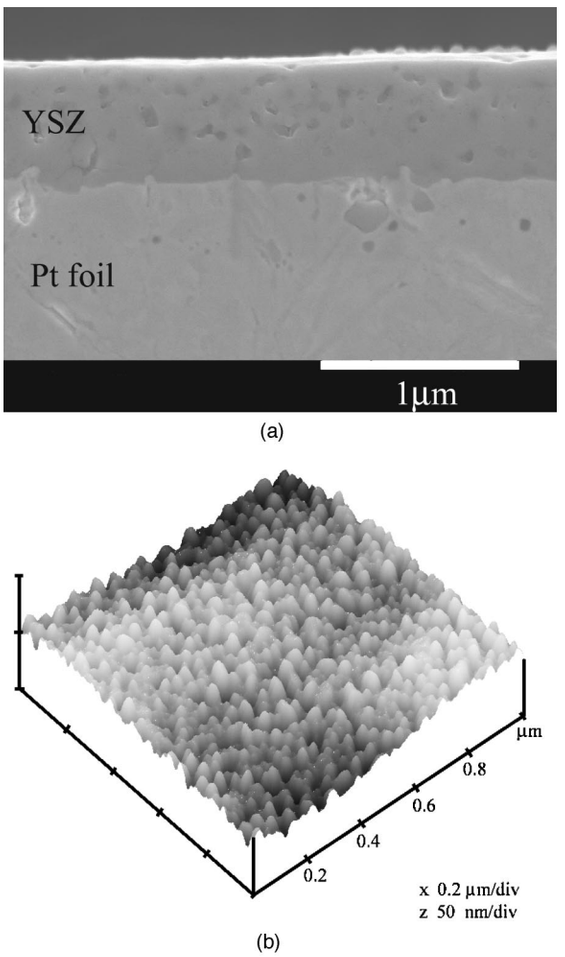

Figure 3. (a, top) SEM image of the cross section and (b, bottom) AFM image of the surface of 1 μm thick YSZ film on Pt foil.

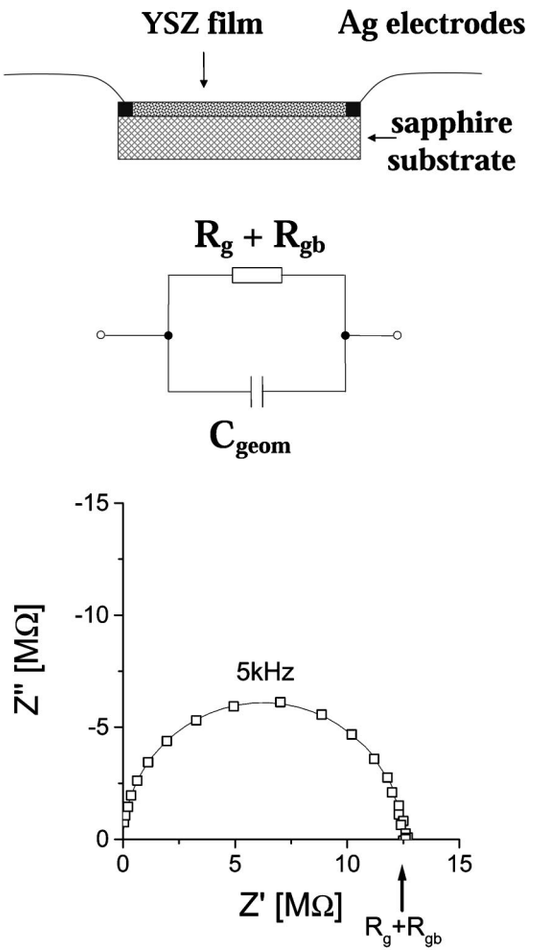

Figure 4. Schematic diagram of in-plane measurement of YSZ film on (a, top) sapphire (b, middle) the equivalent circuit, and (c, bottom) typical impedance spectra at 800°C.

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 Fig. 4a). The small electrode resistance in comparison with the resistance of the material is an advantage in the case of thin-film measurements. However, it is impossible to separate the impact of grain and grain boundary 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 Fig. 4b. 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 Fig. 4c. 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 5 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 the 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

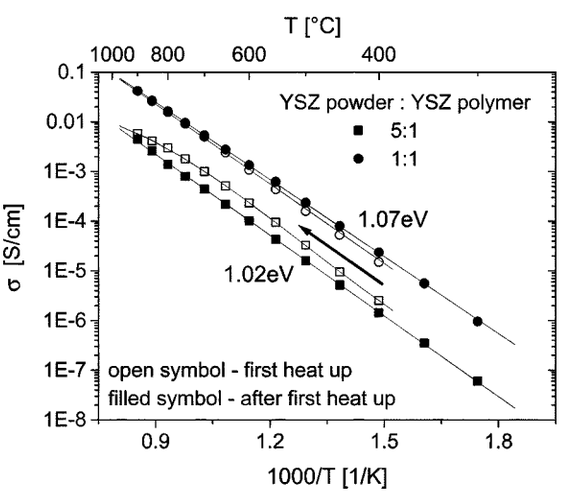

Figure 5. Temperature dependence of conductivity of YSZ film on sapphire.

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 cannot be changed, so crystallization causes 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.[9] The final conductivity (after short time annealing at 900°C) for both specimens is stable and does not change after the subsequent annealing at 900°C. The conductivity and activation energy for the dense film are close to those reported for bulk YSZ.[10]

The measurements on platinum foil substrate were made using in the thickness configuration (Fig. 6a). 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 cannot 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 high and should contain information about the electronic leakage of the film. Figure 6b 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.

Figure 6c and d shows typical impedance spectra obtained for YSZ film on a platinum substrate. In the temperature range from 200-400°C the spectra consists of two closed semicircles (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 (Fig. 6c). When the temperature increases, the impedance spectra shifts to higher frequencies. The grain semicircle shifts out of the measurement range ($f > 1$ MHz) and at 300°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 above 450°C (Fig. 6d). The impedance spectra were fitted to the equivalent circuit presented in Fig. 6b. 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 Fig. 7. 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 agreement with the literature data for bulk YSZ[10] and with that measured in-plane on the sapphire substrate. One may conclude that net shape technology allows the preparation of YSZ films with high ionic conductivity at temperatures as low as 400°C on both sapphire and platinum substrates.

The conductivity related to the blocking effect of the platinum electrode is included in Fig. 7 as well. As previously mentioned the platinum acts as a blocking electrode for oxygen ions, because the oxygen cannot penetrate dense platinum foil. If an ideal blocking effect occurs the vertical line on the impedance spectra should be visible in the low-frequency range.[11] Any sources of the leakage through the film change this phenomenon (nonideal blocking). The nonideal 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 Fig. 8 and are described.

1. 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

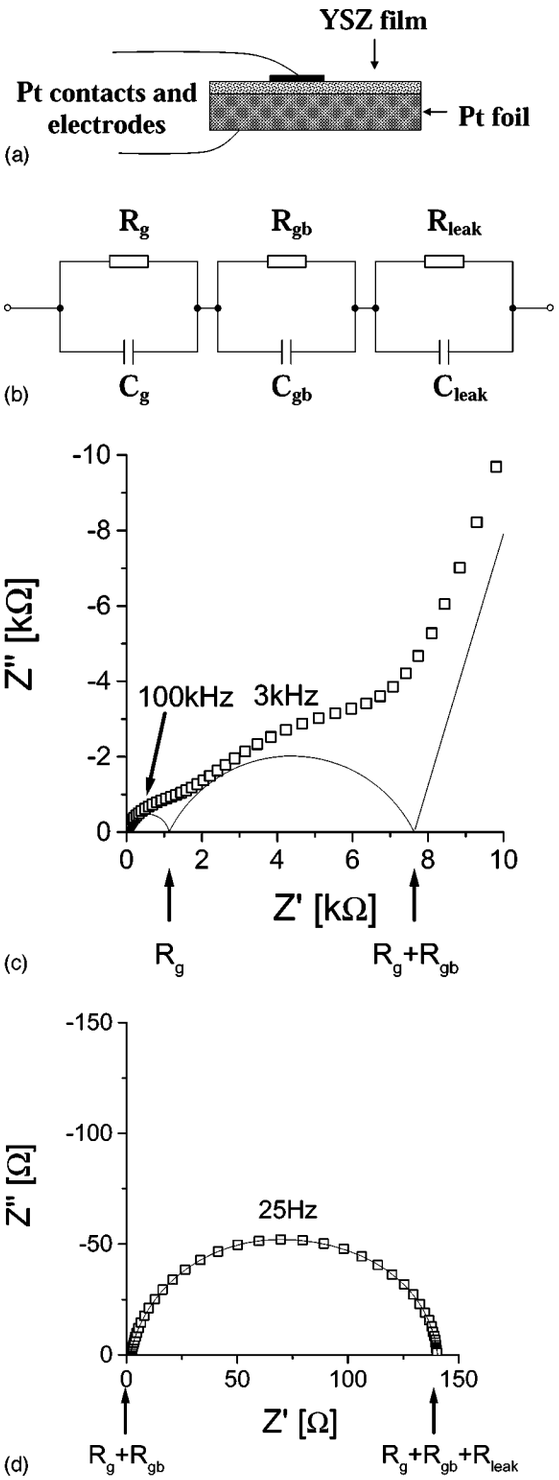

Figure 6. Schematic diagram of measurement configuration through YSZ film on (a, top left) platinum (b, top right) the equivalent circuit (c, bottom left) typical impedance spectra at 300°C and (d, bottom right) at 700°C.

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 small because of the 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

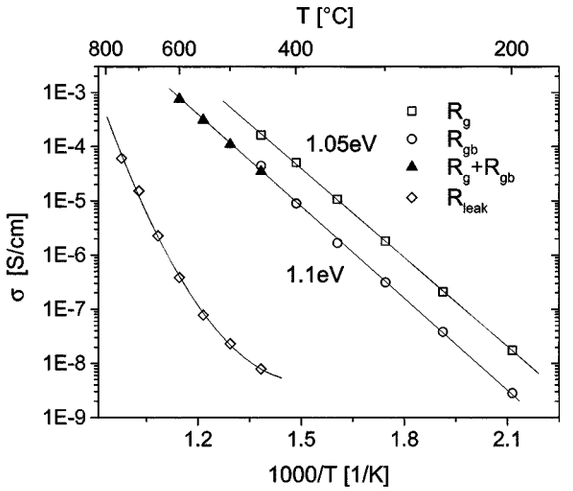

Figure 7. Temperature dependence of conductivity of YSZ film on Pt foil.

leakage is much lower. In addition, the activation energy of about 1 eV should be expected because the leakage is of ionic character, whereas the experimentally observable activation energy is much higher (2.2 eV). So it is possible to conclude that the leakage of the film is not connected with ionic edge leakage.

2. 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 a 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 low, if we are dealing with gas leakage.[12] The experimental value of the activation energy is high (2.2 eV) and does not fit 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 cannot influence the electrical properties of the electrolyte.

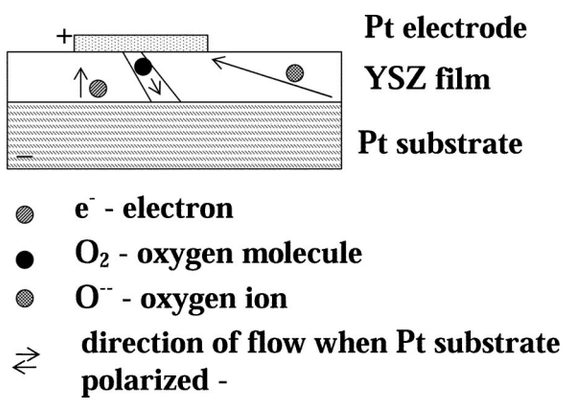

Figure 8. Schematic representation of source of nonideal blocking electrode effects of platinum support.

3. 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 causes the leakage in the sealed structure (electronic leakage). Several authors have measured hole conductivity of the bulk YSZ using different methods.[13-21] The observed values of the hole conductivity and activation energy are widely scattering (E_h differs from 1.5 to 2.4 eV); however, values are in reasonable agreement with calculated activation energy (2.2 eV) 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, because it confirms that dense, high-quality YSZ 1-10 μm thick films can be prepared at temperatures as low as 400°C.

Conclusion

The possibility of using net shape technology for deposition of YSZ film of 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°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.

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