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# Modelling of electrical properties of Ni-YSZ composites

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**Abstract**

Ni-YSZ cermets with tailored microstructural characteristics are of interest in many solid-state electrochemical applications such as fuel cell electrode processes or oxygen sensors. In order to elucidate the role of microstructural parameters on overall Ni-YSZ electrical characteristics, different cermets were synthesized by the citrate–nitrate combustion route and their electrical characteristics were tested. The combustion derived samples exhibited fairly high electronic conductivity, even at a relatively low metal volume fraction of 24 vol.% of Ni. To determine the electrical conductivity behaviour of the composites in a broad range of metal content and its relation to material porosity, the general effective media approach and the sine-wave approximation were used, respectively.


*Keywords:* Ni-YSZ cermets; Electrical conductivity

## 1. Introduction

Electrical multi-phase mixtures or composite materials are widely used in solid-state electrochemical devices such as solid oxide fuel cells (SOFC) and oxygen sensors.[1–3] An electrical composite is defined as a material made up of two or more distinct media, which are arranged in a regular or irregular pattern. The electrical properties (e.g. electrical conductivity) of a given composite may be the average of the different components or may appear through interaction of the separate phases, largely depending on the material microstructure characteristics (grain size distribution, grain morphology, porosity, etc.) and atomistic mechanism (charge carrier mobility, its concentration and hopping rate).[4]

Models of the electrical conductivity of composites have been intensively studied in the past. They can be divided into three classes, i.e., the continuum medium approach based on the Maxwell equation[5] (the Brick-Layer Model—BLM, the Maxwell–Wagner Theory—MWT, Bruggeman's Effective Media Theory—BEMT and McLachlan's Generalized Effective Medium Theory—GEMT),[6–9] the discrete medium approach based on Kirkpatrick's work[10] and the percolation approach for electrical conductivity. Among the mentioned methods for describing the electrical conductivity of anode composites in SOFC applications, the GEMT is particularly interesting. The model takes into account an effective percolation threshold (a critical probability for a continuous conductor or insulator phase throughout the composite) and the effective percolation slope parameter, which determines the steepness in the conductivity versus composition curve around the threshold value.

To describe the relationship between the conductivity of the porous material and its relative density, a novel mathematical approach was proposed.[11] In this innovative interpretation the conductivity of highly porous materials can be expressed by the model of a rotating sine-wave function. By changing the ratio of the contributions of the two sine-waves, one representing the shape of each grain and the other the shape of the bottleneck between particles, the change of electrical conductivity $\sigma$ versus the change of material relative density $\rho/\rho_0$ can be represented.

In SOFC applications, at present Ni/YSZ cermets are the most widely adopted anode materials due to their good electrocatalytic properties against relatively low cost.[12–16] These cermets are normally prepared by mechanical mixing of separately prepared NiO and YSZ oxides, subsequently shaped by various methods such as dry pressing, tape casting, tape calandering, spray printing or hot moulding and finally reduced at high temperatures to form porous Ni-YSZ. The electrical performance of cermets with respect to their geometrical and microstructural details have been investigated by many researchers.[17–26] It was shown that by influencing the final material microstructure, different preparation routes alter the overall electrical properties of the cermet.

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Recently, combustion synthesis was shown to be an attractive method for preparing multicomponent oxide powders that are crystalline, homogeneous and have a narrow particle size distribution.[27–30] Such a reaction takes advantage of the large exothermicity of the reacting redox system, which propagates through the reaction mixture in the form of a self-sustaining front. The propagation speed of the reaction front (0.1–10 cm/s) and reaction temperatures (from several hundred to 2000 or 3000 °C) can be controlled by a variety of appropriate redox systems. Due to the presence of extreme conditions during the synthesis, some unique electrical characteristics of the products obtained were reported in the literature. Anselmi-Tamburini et al. showed that combustion derived Ni/YSZ cermets exhibit relatively high dc conductivity even if the metal content is as low as 20 vol.%.[31]

In this study the citrate (fuel)–nitrate (oxidant) self-sustaining combustion system was used for the synthesis of Ni/YSZ cermets. Metal components forming the final composite are introduced into the system as metal nitrates and due to the relatively high temperature during the combustion, form a very fine mixture of metal oxides. The method is quite simple and does not involve multiple steps.[32] Being a solution process, maximum mixed oxide product homogeneity can be achieved. The microstructure characteristics of the final Ni/YSZ cermets and their conductivity behaviour were studied with respect to the metallic volume fraction in the final materials.

## 2. Experimental procedure

NiO/YSZ composite powders were prepared by a modified combustion synthesis. The combustion system was based on the citrate/nitrate redox reaction. The starting substances for reactive gel preparation were $ZrO(NO_3)_2{\cdot}6H_2O$, $Y(NO_3)_3{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, citric acid and nitric acid (analytical reagent grade). $ZrO(NO_3)_2{\cdot}6H_2O$, $Y(NO_3)_3{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ and citric acid were dissolved separately with minimum additions of water in amounts which assured the desired final nickel content (from 0 to 100 vol.% of Ni in the final cermet, increasing by 5 vol.% of Ni stepwise). $HNO_3$ (aq. 65%) was then admixed with the zirconyl nitrate aqueous solution to ensure an initial citrate/nitrate molar ratio of 0.18. The final YSZ composition after synthesis contained 90 mol.% of $ZrO_2$ and 10 mol.% of $Y_2O_3$. All precursors were mixed together to prepare a solution which was kept over a water bath at 60 °C under vacuum (20 mmHg) until it transformed into a bright green gel. The dried gels were gently milled in an agate mortar and uni-axially pressed (17 MPa) into pellets (16 mm in diameter, height ~30 mm). The pellets were ignited at the top to start a self-sustaining combustion reaction producing NiO/YSZ oxide mixtures. The mixtures of NiO and YSZ were ball milled in ethanol for 3 h and subsequently dried in air for a few hours. Dried powders were shaped into discs (Ø 9 mm, height 6–7 mm) by uni-axial pressing (200 MPa) and then sintered at 1400 °C for 2 h. Final Ni/YSZ cermets were then synthesized by the reduction of NiO/YSZ mixed powders at 900 °C in an $H_2$/Ar atmosphere.

The prepared materials were characterized by the impedance spectroscopy technique. A polythermal quartz cell was employed to perform these tests in the temperature range from 30 to 900 °C in an $H_2$/Ar atmosphere. Impedance was measured using an HP 4284 A analyser over the frequency range from 20 Hz to 1 MHz. Pt paste was used to cover both end surfaces of the discs and applied as electrodes. Samples were polished prior to the microstructure investigations and then examined with scanning electron microscopes (Zeiss Supra 35 VP).

## 3. Results and discussion

In order to achieve good performance by the anode cermet, three main factors have to be considered. The cermet should have high electrical conductivity to reduce the internal ohmic losses during cell operation. Next, the cermet should have enough electrochemical activity to reduce the activation polarization, which is related to the electrochemical reaction at the anode. Lastly, appropriate microstructural characteristics of the cermet are required to reduce the concentration polarization, which is related to the diffusion of the reactants and products of the electrode reaction.

Total resistivities of a series of cermets with different metal content as determined from impedance measurements are shown in Fig. 1. Two groups of cermets with different resistivity versus temperature dependence may be clearly distinguished. In Ni/YSZ cermets with a final Ni content above 24 vol.% resistivity slowly rises with temperature (these cermets exhibit a negative conductivity coefficient). In contrast, cermets with a low Ni content exhibit a positive conductivity coefficient, i.e., resistivity diminishes with temperature. Differences in the resistivity versus temperature behaviour indicate different conductivity mechanisms in the composites. In the group of samples with a negative conductivity coefficient two samples have somewhat higher values of electrical resistivity (samples with 24 vol.% of Ni and 28 vol.% of Ni in the final composite). Despite their higher values of electrical resistivity both samples still exhibit the same reisitivity versus temperature dependence, suggesting that the conductivity mechanism in the samples is the same. The negative conductivity coefficient in these two samples indicates that the Ni phase in the final composite must be a continuous phase although, due to its relative low metal content, the Ni to Ni connection remains relatively poor. If the final metal content does not exceed 24 vol.%, Ni does not form a continuous phase.

The Ni/YSZ volume ratio dependence on composite conductivity is shown in Fig. 2. The conductivity of the cermets increases as the Ni content in the cermet is increased. A sudden rise in conductivity versus Ni content was found at approximately 25 vol.% Ni, indicating a change in the conductivity mechanism. On exceeding the above-mentioned Ni content value the conductivity of the cermets reaches a maximum and does not change much with increasing Ni content. In the same way, cermets with a Ni content lower than 25 vol.% exhibited relatively low but similar $\sigma$ values. The characteristic shape of the conductivity versus Ni content curve shows typical percolation phenomena and is similar to the shape reported by Dees et al.,[12] except that our absolute values of conductivity were smaller. The difference between the data may be ascribed to poor sintering

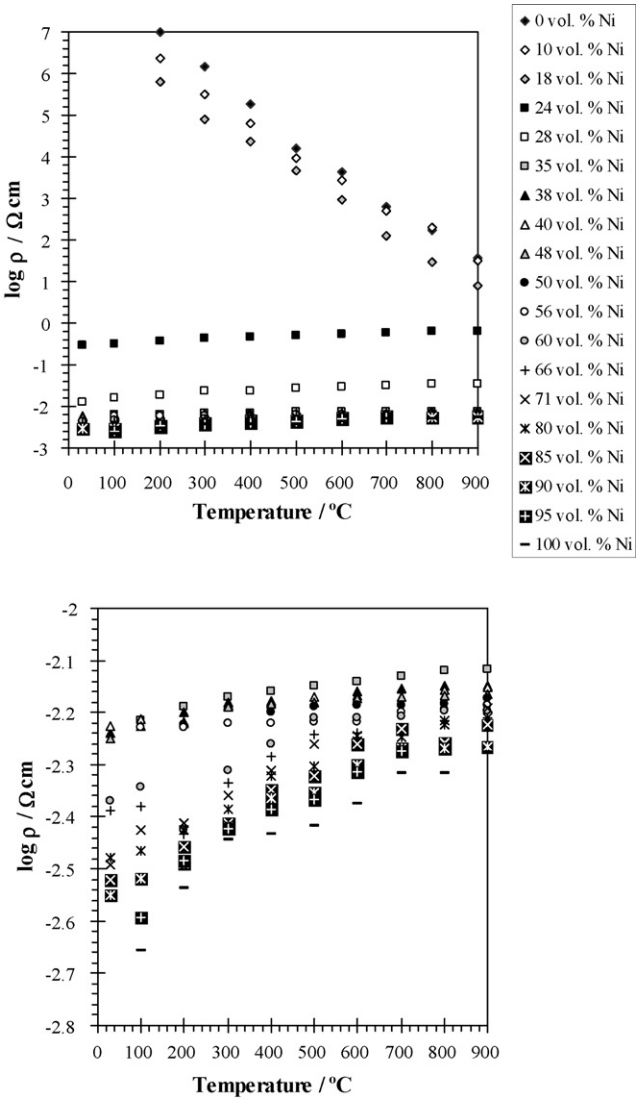


Fig. 1. Resistivity vs. temperature for a series of cermets with different metal content in the final product, as denoted in the legend.

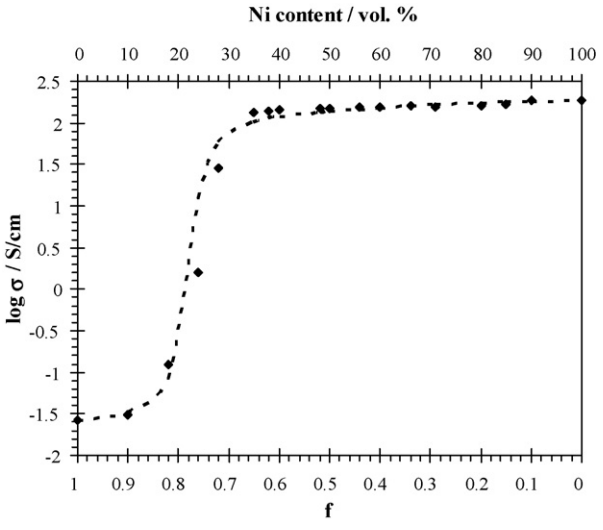


Fig. 2. Dependance of Ni/YSZ volume ratio on conductivity of the cermet at 900 °C (marked values) and predicted trend using GEMT model (dashed line).

of the cermets when they are prepared from combustion derived powders.

As a quantitative model to relate microstructure with electrical properties of composite materials we used the GEMT approach.[9] The general form of the GEMT equation can be written as:

$$\frac{f(\sigma_l^{1/t} - \sigma_m^{1/t})}{\sigma_l^{1/t} + (f_c/(1-f_c))\sigma_m^{1/t}} + \frac{(1-f)(\sigma_h^{1/t} - \sigma_m^{1/t})}{\sigma_h^{1/t} + (f_c/(1-f_c))\sigma_m^{1/t}} = 0$$

where $\sigma_l$, $\sigma_h$ and $\sigma_m$ are the conductivities of the poorly conducting phase, the highly conducting phase and the composite material, respectively, $f$ the volume fraction of the insulating phase, $f_c$ the fraction corresponding to the percolation threshold and $t$ is a system-specific parameter. As limiting values – the conductivities of 10 mol.% YSZ $\sigma_l$ and pure nickel $\sigma_h$ – we used the measured conductivity values at 900 °C of samples with 0 vol.% Ni ($\sigma_l = 0.026$ S/cm) and 100 vol.% Ni ($\sigma_h = 189.234$ S/cm). By fitting the conductivity versus Ni content data to the GEMT equation, the optimized parameters $f_c$ and $t$ were calculated to be 0.75 and 0.66, respectively. These results reveal that the conductivity threshold value $f_c$ is close to a typical value of a composite material (≈1/3 volume fraction of the highly conductive phase), while the parameter $t$ shows an untypical low value, indicating a relatively narrow region where the change in the conductivity mechanism occurs (typical values of parameter $t$ fall in the range 1.2–1.6). The GEMT calculated conductivity curve matches relatively well with the measured values (Fig. 2). A slight mismatch around the threshold value could be ascribed to the fact that GEMT theory presumes a rather ideal situation where particles are of similar sizes, spherical and isotropic, which is not always the case in real samples.

The relatively low calculated $f_c$ value could be related to the peculiarity of the cermet microstructure obtained by the combustion method. Cermets obtained by the citrate–nitrate combustion route are submitted during synthesis to extreme conditions. In the reacting zone the temperature rises rapidly (heating rate ~450–500 °C/s) reaching its final value of 1100–1180 °C in approximately 2 s. High temperatures and a short reaction time ensure a nearly ideal random phase distribution in the prepared products where different phases are mixed on a very low-scale (one-phase dominance is normally rather below 100 nm). During subsequent sintering the one-phase dominance is coarsened but still remains in the sub-micron range in the final cermets. In such a microstructure the presence of a long percolation path of the metallic phase is highly probable, even near the theoretical threshold value.

The apparent conductivity of sintered materials is sensitive to their relative density or porosity. The relationship between relative conductivity ($\sigma/\sigma_0$) and relative density ($\rho/\rho_0$) or porosity ($\varepsilon$) for two cermets, one with a low Ni content and the other rich in Ni, is demonstrated in Fig. 3. The relative densities of the two cermets were altered by submitting the samples to different sintering temperatures from 1000 to 1450 °C and are presented in Table 1. Because the final step in cermet preparation is reduction of NiO to Ni, which is always accompanied by an increase in material porosity, fully dense cermets cannot be prepared using

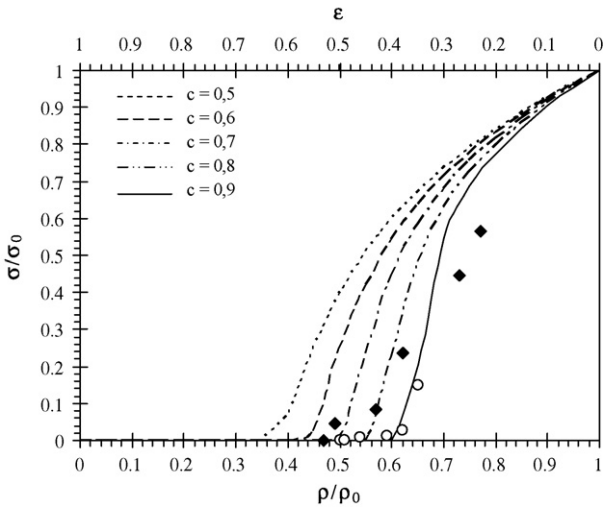


Fig. 3. Calculated relationships between relative density $\rho/\rho_0$ or porosity $\varepsilon$ and relative conductivity $\sigma/\sigma_0$ for different values of $c$; (solid, dashed and dotted lines as described by Mizusaki et al.[11]) and observed trend of the measured data ((♦) 10 vol.% Ni and (◯) 50 vol.% Ni).

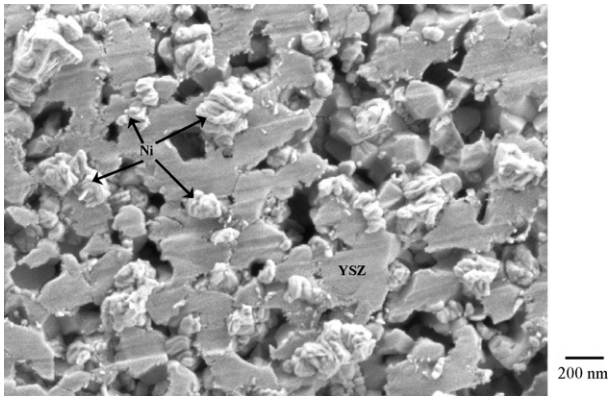


Fig. 4. Microstructure of 10 vol.% Ni sample (Ni particles in the composite are represented as isolated islands—particles with a wrinkled surface).

the described preparation method. For that reason, prior to relative conductivity calculation, $\sigma_0$ values were estimated using the GEMT equation (10 vol.% Ni; $\sigma_0 \sim 0.07$ S/cm, 50 vol.% Ni; $\sigma_0 \sim 6000$ S/cm). As limiting values $\sigma_l$ and $\sigma_h$ for $\sigma_0$ estimation the conductivities of pure YSZ (10 mol.% $Y_2O_3$) and Ni at 900 °C ($\sigma_l \sim 0.05$ S/cm and $\sigma_h \sim 12000$ S/cm) were taken, while parameters $f_c$ and $t$ were used as calculated above.

The results found for the dependence of relative conductivity on relative density for the two samples are essentially consistent with the sine-wave approximation of conductivity change for porous materials proposed by Mizusaki et al.[11] Scattering of the observed results around the theoretically predicted curves may be attributed to the inaccuracy of the conductivity measurements, or some microstructural defects in the measured bodies, such as micro-cracks, low-scale material inhomogeneity, inhomogeneous grain size and shape or local packing disorder. Comparison of the results presented in Fig. 3 and in Table 1 revealed that composite relative conductivity converges to 0 if the sintering temperature does not exceed 1000 °C. 1000 °C is a relatively low temperature for NiO/YSZ sintering where the densification process is just starting (relative shrinkage of the sample with 10 vol.% Ni at 1000 °C was only 1.5%, while densification of the 50 vol.% Ni sample begins somewhat earlier and at 1000 °C reaches 3.8%). Low sintering temperatures mean that the material's sintered densities remain very close to the material's green density. Since the usually attained density of green bodies is 40–60% of the theoretical density, particles remain isolated except for point-contact between them. During reduction at 900 °C NiO transforms to Ni, which may lead to subsequent Ni particle sintering but, on the other hand, Ni formation always increases composite porosity, again reducing particle-to-particle contact. These two opposite effects probably mean that in such highly porous bodies even in reduced samples particle-to-particle contact does not change significantly. Electric conduction in the case of limited contact between the particles is thus strongly hindered. With increasing sintering temperature the relative composite sintered densities increase, ensuring better contact between particles which is also preserved after reduction and can be demonstrated through higher relative conductivities. The highest relative reduced densities obtained remained relatively low (especially in the case of the 50 vol.% Ni sample). Therefore, the consistency of the obtained $\sigma/\sigma_0$ versus $\rho/\rho_0$ relationship in the high density region was not defined.

Two cermet microstructures sintered at 1400 °C and then reduced at 900 °C are shown in Figs. 4 and 5. Ni particles in these two pictures are represented as grains with a wrinkled surface, while YSZ particles have a smooth surface. The average grain size of Ni particles varies from approximately 100–300 nm (10 vol.% Ni sample) to 100 to several hundreds nanometer range (50 vol.% Ni sample). In the case of the 50 vol.% Ni sam-

Table 1
Densification properties of selected Ni/YSZ cermets

| Sample | Temperature (°C) | | | | | |
|---|---|---|---|---|---|---|
| | 1000 | 1100 | 1200 | 1300 | 1400 | 1450 |
| 10 vol.% Ni | | | | | | |
| Relative sintered density, $\rho_{sint.}$ (%) | 0.49 | 0.52 | 0.64 | 0.69 | 0.85 | 0.89 |
| Relative reduced density, $\rho_{red.}$ (%) | 0.47 | 0.49 | 0.57 | 0.62 | 0.73 | 0.77 |
| 50 vol.% Ni | | | | | | |
| Relative sintered density, $\rho_{sint.}$ (%) | 0.52 | 0.54 | 0.68 | 0.79 | 0.89 | 0.91 |
| Relative reduced density, $\rho_{red.}$ (%) | 0.50 | 0.51 | 0.54 | 0.59 | 0.64 | 0.65 |

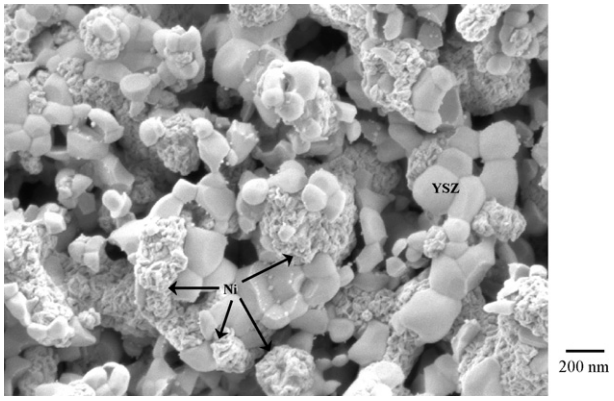


Fig. 5. Microstructure of 50 vol.% Ni sample (particles with a wrinkled surface in the composite are Ni particles; YSZ particles in the composite have a smooth surface).

ple metallic particles tend to link and form a continuous network. In some spots Ni particles cover the surface of the YSZ. On the contrary, in the case of the 10 vol.% Ni sample they are isolated and separated by the ceramic phase.

The presented microstructures of the two samples correspond well with the cermets' electrical properties. Increasing values of electrical conductivity with increasing temperature in the case of the 10 mol.% Ni sample can be explained by the fact that YSZ phase is a continuous phase throughout the sample. On the other hand, when both metallic and ceramic phases form continuous networks (50 vol.% Ni sample), the chief path of conduction is through the Ni phase and the apparent cermet electrical conductivity decreases with increasing temperature, which is indicative of a metallic electronic conductor.

## 4. Conclusions

Citrate–nitrate combustion synthesis was shown to be an attractive method for the preparation of Ni/YSZ cermets with interesting electrical properties. The cermets generally exhibit a good dispersion of metal in the ceramic matrix. The microstructural characteristics such as porosity and the densification process of the cermets can be controlled to some extent by varying the cermets' chemical composition. The dependence of electrical conductivity on Ni content shows a relatively sharp transition in conductivity mechanism at around 25 vol.% Ni in the cermet. The relative conductivity of the final Ni/YSZ cermets is sensitive to the dependence of porosity on relative density and is consistent with the sine-wave approximation of conductivity change for porous materials.

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