Optimization of Ni-YSZ Solid Oxide Fuel Cell anodes by surface laser melting

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A cermet composed of a metallic component (nickel) and a ceramic matrix (yttria stabilized zirconia) is commonly used as the anode for Solid Oxide Fuel Cells (SOFC). In the present work we intend to improve the performance of Ni-YSZ anodes by surface laser melting. Symmetrical cells, consisting of two NiO-YSZ anodes ($\sim 20\text{ }\mu\text{m}$ thickness) separated by a relatively thin YSZ electrolyte ($\sim 500\text{ }\mu\text{m}$) were fabricated by convectional ceramic techniques. Subsequently, laser melting treatments of both anodes were performed using a CO_2 laser system, producing a NiO-YSZ eutectic lamellar microstructure. Laser power of 100 W and processing rates of 1 mm s^{-1} were determined as the optimum processing conditions. Symmetrical processed plates (eutectic sample) were electrically characterized by impedance spectroscopy (EIS), and the results were compared with non-processed plates (ceramic sample). Preliminary EIS results showed that the polarization resistance at higher temperatures (in the range of $900\text{ }^\circ\text{C}$) is about $0.5\text{ }\Omega\text{cm}^2$ for both the eutectic and the ceramic sample. However, at lower temperatures (in the range of $800\text{ }^\circ\text{C}$) the polarization resistance for both samples differs considerably (2.9 and $1.6\text{ }\Omega\text{cm}^2$ for the ceramic and eutectic sample, respectively). These experiments confirmed that optimization of the microstructure by laser surface treatment plays a crucial role in the electrochemical properties of the anode cermets.

Keywords: NiO, Yttria stabilized zirconia, eutectic, Solid Oxide Fuel Cells, laser processing

Introduction

The typical material used as solid oxide fuel cell (SOFC) fuel electrode for both fuel cell and electrolysis applications is a cermet composed by an ionic conductor phase (YSZ: yttria stabilized zirconia) and a metallic phase (nickel).^{1,2} However, the current state of the art material presents some disadvantages including poor redox stability, low tolerance to sulphur, nickel coarsening after long-term operation and carbon deposition when using hydrocarbon fuels.³ The current problems could be avoided by either using alternative materials⁴ or by improving the present Ni-YSZ materials. For example, a composite Cu–CeO₂–YSZ/SDC anode demonstrated that the addition of CeO₂ to Cu–YSZ/SDC cermet significantly enhanced the performance of the cell, especially for hydrocarbon fuels.⁵ However, one problem associated when using hydro-carbon fuels is that most of those fuels contain sulphur compounds as minor products, which are easily converted to hydrogen sulfide (H₂S) upon reforming, and thus deactivating the Ni-YSZ cermet.⁶ Another problem associated with Ni-YSZ anodes is the accidental reoxidation of Ni to NiO, producing a microstructural irreversibility during the redox process and leading to strain accumulation, over several redox cycles.⁷ In order to solve this problem, infiltration of Ni metallic particles into porous YSZ have been proposed as a possible solution.^{8,9} Finally, last problem of Ni-YSZ cermets is related to Ni agglomeration during cell operation. This process is accelerated by the poor wettability between metallic Ni and the ceramic YSZ phase.¹⁰ It has been reported significant microstructural changes in the anode Ni phase over a range of operational times, including phase size growth and changes in connectivity, interfacial contact area and contiguous triple-phase boundary (TPB) length.¹¹ A possible solution is the use of channelled Ni–YSZ anodes produced from NiO–YSZ

directionally solidified eutectics (DSE).¹² The low-energy interfaces formed between the phases ensure good stability of the material over time. It was reported that the channelled microstructure of this cermet improves the performance of the anode, allowing good gas flow and electronic conduction through the Ni porous lamellae.^{13, 14, 15} However, although the advantages of the cermet material were demonstrated, the fabrication of a SOFC single cell containing a channelled cermet is still a challenge for practical applications, as a dense electrolyte needs to be deposited on top of a fully dense material. Garcia *et al.* showed that it is possible to fabricate dense YSZ films (from 5 to 10 μm thick) by PI-MOCVD (pulsed injection metal organic chemical vapour deposition) on NiO-CaSZ (calcia stabilized zirconia) eutectics.¹⁶ In a similar approach, Merino *et al.*¹⁷ proved that applying surface laser melting to YSZ rich hypereutectic of YSZ–NiO ceramics, it is feasible to obtain layered material consisting of different layers: primary zirconia, eutectic with graded composition and single NiO phase. Once more, the fabrication of a SOFC cell by this procedure is still challenging.

The objective of the present work is the fabrication of an electrolyte supported SOFC where the Ni-YSZ electrodes are produced from DSE using laser assisted techniques. Laser processing was previously used for SOFC applications including fabrication of Ni, Co and Mn-YSZ eutectics,^{15,18,19} drilling of Ni-YSZ supports,²⁰ laser machining of self-supporting YSZ electrolytes²¹ or micro- solid oxide fuel cells fabricated by pulsed laser deposition (PLD) techniques.²² In this work, Ni-YSZ/YSZ/Ni-YSZ symmetrical cells will be fabricated by conventional ceramic methods. Subsequently, laser melting treatments of both sides will be performed using a CO₂ laser system, producing a NiO-YSZ eutectic lamellar microstructure. Symmetrical processed samples (eutectic) will be

characterized by impedance spectroscopy, and the results will be compared with non-processed samples (conventional ceramic cermets).

2. Materials and methods

2.1. Sample fabrication

2.1.1. Fabrication of the electrolyte supports

YSZ ceramic substrates were fabricated by uniaxial pressing of YSZ powders (8 mol% yttria stabilized zirconia, TZ-8Y, Tosoh, Japan) with a mean particle size of 0.2 μm , using poly-vinyl alcohol (PVA) as a binder, at 5 MPa. Green substrates were subsequently sintered at 1400 °C during 2 hours, achieving relative densities between 96% and 99%. Final dimensions of the substrates after sintering are approximately: 20 x 8 x 0.5 (in mm).

2.1.2. Symmetrical cells fabrication

NiO-YSZ suspensions were fabricated using 8YSZ (8 mol% yttria stabilized zirconia, TZ-8YS, Tosoh, Japan) with a mean particle size of 0.5 μm , and NiO (Alfa Aesar GmbH & Co. KG, Germany) with a mean particle size of less than 44 μm . NiO powders were previously milled in an attrition mill for 2 hours using 2-propanol as solvent, in order to obtain a mean particle size of 1.2 μm . Particle size of the powders was determined using Dynamic Light Scattering (DSL) (Malvern Instruments Ltd, United Kingdom). Corn-starch was also used as a pore former, as porosity will help to dissipate heat and reduce thermal shock during laser treatments. Powders were finally mixed in ethanol media, using PVB (polyvinyl butyral) as binder and Beycostat as dispersant agent. In

order to optimize slurry compositions, rheological measurements were performed using a rotational rheometer equipped with the Rheowin software (Haake Mars, Thermo Scientific, Germany). The measurements were performed operating in control rate (CR) mode at 20 °C, and the conditions were from 0 to 1000 s⁻¹ in 150 seconds, maintaining at this rate for 30 seconds and coming back to 0 s⁻¹ at the same rate. Finally, YSZ ceramic substrates were dip-coated into the NiO-YSZ slurries. Four dip-coatings, drying at ambient air for 30 minutes between each dip, were needed to obtaining the desired anode thicknesses. Samples were finally sintered at 1350 °C for 2 hours, obtaining typical NiO-YSZ thicknesses in the range of 20 µm.

2.1.3. Laser assisted directional solidification

Laser surface melting was performed using a commercial pulsed CO₂ laser (Marcatex Flexi 250, 10.6 µm wavelength). Samples were placed on a metallic support inside of a furnace at temperatures in the range of 1000 °C in order to reduce the thermal shock during resolidification. The melting temperature of the NiO-YSZ eutectic (~1850 °C) was directly measured using a MINOLTA Land Cyclops 52 optical pyrometer.¹⁵ A homogeneous intensity laser line (10x1 mm size) was focussed on the surface of the sample, travelling at speeds varying from 1 to 10 mm/s along the Y direction. The treatment time for each anode of a typical sample is less than 30 seconds. Laser powers from 75 to 160 W were used. Frequencies as high as 20 KHz were used in order to resemble the pulsed laser to a continuous laser.²³ All laser parameters were controlled using the *Easy Mark 2009* software. Additional details about laser surface melting of similar samples can be found in 17, 24.

2.2. Microstructural and electrical characterization

Microstructural analysis was performed using a field emission scanning electron microscope (FE-SEM) from Carl Zeiss, Germany (Merlin FE-SEM). Electrical characterization of the symmetrical cells was performed by electrochemical impedance spectroscopy (EIS) analysis. Samples were mounted in a spring-loaded test rig, designed and built in-house, using Pt mesh as current collectors. NiO paste (in-situ reduced to metallic Ni) was applied to both sides of the pellets to improve current collection. The typical surface area of the anodes is 0.8 cm². AC impedance measurements were recorded using a VSP impedance analyser (Princeton Applied Research, Oak Ridge, USA) in the frequency range of 10⁵ Hz to 0.1 Hz using an electrical perturbation of 20 mV. The data obtained was finally analysed using the Z-Plot/Z-View software package (Scribner Associates, Southern Pines, NC, USA).

3. Results and discussion

3.1. Symmetrical cells fabrication

NiO-YSZ suspensions were firstly optimized. The selected composition of the precursor ceramics are (mol%): 75 NiO–25 YSZ (5 mol% extra of NiO is needed to compensate NiO evaporation during the melting process).¹⁵²⁵ As discussed in the experimental section, 15% of corn-starch (in vol%) was introduced as pore former to reduce thermal stress. Based on previous studies for NiO-YSZ²⁶ and LSM-YSZ²⁷ similar compositions, we have fabricated suspensions of 10% of solid load in ethanol media using 5% of binder (PVB) and 1% of dispersant (Beycostat). The measured viscosity of the suspensions was 0.03 Pa s⁻¹. After this, YSZ ceramic substrates were dip-coated into the NiO-YSZ slurries, obtaining typical NiO-YSZ thicknesses after sintering in the range of 15-20 μm, as observed in figure 1.

3.2. Laser processing

The parameters used for the laser surface melting of the samples are summarized in table 1. Two key parameters need to be controlled: the traverse speed (V) of the sample and the power of the CO₂ laser system. By increasing the speed of the sample, the solidification rate will be increased and as a consequence the interlamellar spacing (λ) of the eutectic microstructure will be reduced.¹² The relationship between λ and V according with the Hunt–Jackson law is described in equation (1).²⁸

$$\lambda V^2 = \text{Constant} \quad (1)$$

Considering the experimental interlamellar spacing founded by Dhalenne *et al.*²⁹ and Merino *et al.*¹⁴ for the NiO-CaSZ (calcia stabilized with zirconia) system, this constant is about 129 $\mu\text{m}^2 \text{ mm h}^{-1}$. According with this value, an interlamellar spacing in the range of 200 nm is expected for processing rates of $\sim 1 \text{ mm s}^{-1}$. The laser power is the additional parameter to be controlled, as it is necessary to completely melt the NiO-YSZ coating without damaging the YSZ substrate. As observed from table 1, best conditions were found for traverse speed of 1 mm s^{-1} and laser power of 100 W (samples 1.4, 2.1 and 2). Typical microstructures for the different samples are shown in figure 2. Sample 1.1 showed partial sintering of the anode coating due to insufficient laser power (75 W) for that traverse speed (1 mm s^{-1}). By increasing laser power by a factor of 2 using the same rate (sample 1.2, 150 W) the total NiO-YSZ coating was melted. However, the microstructure showed NiO-YSZ eutectic regions and segregation of primary phase of YSZ, especially near the YSZ support. Due to the higher laser power, nickel oxide was evaporated in excess during the melting process, and YSZ primary phase was segregated to compensate the evaporation. Finally, optimum

conditions were founded for intermediate laser powers (100 W: sample 2.1), mainly showing the NiO-YSZ eutectic as observed in figure 2. In order to get a finer microstructure, several attempts were also performed at 2 mm s⁻¹. As observed for sample 2.3, 100 W was insufficient to melt all the NiO-YSZ coating. By increasing the laser power to 135 W (sample 2.4, microstructure shown in figure 2), all the coating was melted and the microstructure showed eutectic microstructure and segregation of both NiO and YSZ. If we compare this microstructure with sample 1.2, in this case as the traverse speed was increased by a factor of 2, possibly there was not enough time for NiO evaporation and it segregated as primary phase. In general, during the experiments listed in table 1 we observed more superficial cracks in samples processed at higher rates. For that reason the processing parameters for 2 mm s⁻¹ were not further optimized and the subsequent study will be performed with samples processed at 1 mm s⁻¹. As observed from figure 2, image analysis for sample 2.1 showed an interlamellar spacing (λ) of ca. 286 nm, and the thickness of each phase was ca. 90 nm and 200 nm for the YSZ and NiO, respectively.

After optimization of the laser processing parameters, NiO-YSZ/YSZ/NiO-YSZ symmetrical cells were laser processed on both sides. From now on, the processed sample will be referred as eutectic sample. Non-processed samples (will be referred as ceramic samples) were also fabricated for comparison. All symmetrical cells were then firstly reduced at 800 °C under humidified hydrogen atmosphere. Typical microstructures for both ceramic and eutectic samples after reduction are shown in figure 3. It is expected that the channelled microstructure of this cermet will improve the performance of the anode, allowing good gas flow and electronic conduction through the Ni porous lamellae. In addition, as previously reported for Ni-YSZ samples

produced from reduction of NiO-YSZ eutectic compositions, aging experiments under a continuous flow of dry H_2/N_2 for 300 h at 900 °C showed that the low-energy interfaces formed between YSZ and NiO phases ensure good stability of the material over time.¹³ Nickel connectivity within the cermet was also analysed. In fact, SEM images shown in figure 3 are collected using an InLens secondary electron detector, using acceleration voltages in the range of 1 kV. By this analysis it is possible to distinguish between percolating and non-percolating nickel.³⁰ This is clearly observed from figure 3 that the eutectic sample presents much better connectivity between nickel metallizing particles, due to the finer and well-aligned microstructure.

3.3. Electrical characterization

Finally, both ceramic and eutectic samples were preliminarily characterized by EIS measurements. Note that the thickness of the functional electrodes of the symmetrical thickness is between 8 to 15 μm . This is a non-optimized parameter, as the electrochemical active area of a Ni-YSZ anode could be up to 30 μm .³¹ Typical Nyquist plots are shown in figure 4. For clarification purposes, ohmic contributions were subtracted and the polarization resistances were divided by two in order to account each electrode. According with literature data,³² the impedance response of the hydrogen/water reaction on Ni-YSZ cermet electrodes at OCV (open circuit voltage) involves up to three processes with different dependencies on temperature and the partial pressure of the reactants. At temperatures below 845 °C, the impedance was found to be charge-transfer controlled. The capacitances of this contribution appear in the range of $\sim 10^{-4} \text{ F cm}^{-2}$, and this parameter is very dependent to the microstructure.

At temperatures above 890 °C, two reaction steps, charge transfer and adsorption due to a high fractional surface coverage, determine the overall reaction rate. Similar findings were reported by Primdahl *et al.*³³ They reported that the high frequency (HF) contribution is the only one microstructure dependent and it is attributed to a combination of resistance of charge-transfer from Ni to YSZ and oxide ions resistance in YSZ particles in the cermet. In addition, based in the literature, activation energies for Ni–YSZ electrodes ranged from 0.7 to 1.8 eV depending on the geometry, sintering temperature and raw materials employed.³⁴

In our experiments (fig. 4), Ni-YSZ polarization resistance is thermally activated and decreases with temperature, as expected. In addition, polarization resistances for both the eutectic and ceramic samples are rather similar at the high temperature range (900-950 °C). However, significant differences are observed when decreasing the operation temperature, where the polarization resistance decreases for the eutectic sample. As observed in figure 4, the experimental data was fitted using two R-CPE components, as shown in the inset of the figure. R1 component is appearing at high frequencies (HF) and R2 at low frequencies (LF). In concordance with previous studies reported in the literature, R1-HF component was attributed to the microstructure of the cermet and R2-LF component was attributed to surface adsorption. At temperatures below 850 °C, the microstructure of the anodes (charge-transfer controlled, R1-HF) plays a crucial role in the polarization resistance. Due to the well aligned and dispersed microstructure of the eutectic sample, R1-HF component significantly decreases at lower temperatures. All the analysed parameters are summarized in table 2. As observed, R2-LF component is about constant for both samples, whereas R1-HF component decreases considerably for the eutectic sample.

The activation energy for the ceramic sample (1.86 eV) is slightly higher than those reported in the literature possibly due to the small thickness of the functional electrode ($\sim 10\text{ }\mu\text{m}$). Although the thickness of the eutectic sample is in the same range, the activation energy is significantly reduced (1.31 eV) as a consequence of the well aligned microstructure. As observed from table 2, the polarization resistance is reduced by approximately a factor of two at temperatures close to 800 °C.

4. Conclusions

Optimization of laser processing parameters was performed in order to fabricate NiO-YSZ/YSZ/NiO-YSZ symmetrical cells, where the NiO-YSZ layers ($\sim 20\text{ }\mu\text{m}$ thickness) possess an eutectic lamellar microstructure. Optimum laser conditions were founded for laser powers of about 100 W and processing rates of 1 mm s^{-1} . Symmetrical non-processed samples were also fabricated for comparison purposes. Polarization resistance at higher temperatures (in the range of 900 °C) was found to be similar for both samples (about $0.5\text{ }\Omega\text{cm}^2$). However, at lower temperatures ($\sim 800\text{ }^{\circ}\text{C}$) the polarization resistance of the eutectic sample is significantly smaller ($1.6\text{ }\Omega\text{cm}^2$) than the ceramic sample ($2.9\text{ }\Omega\text{cm}^2$) due to the well-aligned microstructure for the eutectic sample. Although these experiments need to be confirmed by optimized cells with thicker electrodes, it is demonstrated that optimization of the microstructure is essential to improve the electrochemical properties of electrodes, and thus reducing the operation temperature of SOFC devices.

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Table 1. Summary of the laser processed samples.

Sample code	Traverse speed (mm s ⁻¹)	Laser power (W)	Results
1.1	1	75	Sintering of the layer (no melting)
1.2	1	150	Total melting. Some cracks YSZ primary phases + eutectic zones
1.3	10	100	Sintering of the layer (no melting)
1.4	1	100	Total melting. No cracks Majority of eutectic microstructure
2.1	1	100	Total melting. No cracks Majority of eutectic microstructure
2.2	1	100	Total melting. No cracks Majority of eutectic microstructure
2.3	2	100	Partial melting
2.4	2	135	Total melting. Severe cracks NiO and YSZ primary phases + eutectic zones
2.5	2	145	Total melting. Severe cracks NiO and YSZ primary phases + eutectic zones
2.6	2	160	Total melting. Severe cracks NiO and YSZ primary phases + eutectic zones

Table 2. Resistances obtained by fitting the experimental EIS data for the eutectic and ceramic samples at the studied temperatures.

Sample	Temp. (°C)	R1 (Ωcm ²)	R2 (Ωcm ²)	ASR (Ωcm ²)	Sample	Temp. (°C)	R1 (Ωcm ²)	R2 (Ωcm ²)	ASR (Ωcm ²)
Ceramic	815	2.49	0,41	2.90	Eutectic	810	1.19	0.42	1.61
	840	1.72	0.24	1.96		840	1.07	0.29	1.36
	875	1.06	0.12	1.18		870	0.84	0.20	1.04
	906	0.68	0.08	0.76		901	0.58	0.16	0.74
	925	0.51	0.07	0.58		917	0.43	0.15	0.58
	943	0.43	0.06	0.49		937	0.33	0.13	0.46
	E_a (eV)			1.86		E_a (eV)			1.31

Figure 1. SEM image (transverse cross-section) showing a porous NiO-YSZ anode deposited on top of a YSZ electrolyte. Arrows indicate the additional porosity caused by the pore former.

Figure 2. SEM images (transverse cross- sections) of different surface laser treatments.

Brightness scale: YSZ (dark phase) and NiO (light phase).

Figure 3. SEM images (transverse cross- sections) for the ceramic (left) and eutectic (right) samples after reduction. Brightness scale: YSZ (dark phase) and NiO (light phase).

Figure 4. EIS impedance analysis for the eutectic and ceramic sample at 810 and 815 °C, respectively. The equivalent circuit shown in the inset was used to fit (solid line) the experimental data (open circles and squares).

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