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Corresponding Author: Dr. Daniel Marinha, PhD

Corresponding Author's Institution: Saint-Gobain

First Author: Daniel Marinha, PhD

Order of Authors: Daniel Marinha, PhD

Abstract: Composites of 8 mol% Yttria-stabilized Zirconia (YSZ) containing 0, 7, 10 and 14 vol.% of graphene nano-platelets (GNP) were fully densified by Spark Plasma Sintering. The effect of GNP on the electrical performance of the composites was analyzed by impedance spectroscopy as a function of temperature (150 - 800 °C) and oxygen partial pressure (0.21 - 10-20 atm). Results show that below GNP percolation threshold (7.1 vol.%), the electrical behavior is dominated by the matrix oxygen-ion conductivity. Above the threshold, the conductivity is predominantly electronic provided by the GNP network. The total conductivity of composites was used as an indicator of GNP stability in different atmospheres. YSZ/GNP composites remain stable in inert conditions up to 600 °C, and in reducing conditions up to 800 °C, making them good alternatives to perovskite-based materials used for electrochemical applications.

Suggested Reviewers: Cesar Steil
marlu-cesar.steil@lepmi.grenoble-inp.fr

Jérôme Chevalier
jerome.chevalier@insa-lyon.fr

Filipe Figueiredo
lebre@ua.pt

Mixed-ionic and electronic conduction properties and stability of YSZ-graphene composites

Authors: Daniel Marinha^{1,*} Manuel Belmonte²

¹ LSFC Laboratoire de Synthèse et Fonctionnalisation des Céramiques, UMR 3080, CNRS/Saint-Gobain
CREE, 550 Av. Alphonse Jauffret, 84306 Cavaillon Cedex, France

² Institute of Ceramics and Glass (ICV-CSIC), Kelsen 5, 28049 Madrid, Spain

Abstract

Composites of 8 mol% Yttria-stabilized Zirconia (YSZ) containing 0, 7, 10 and 14 vol.% of graphene nano-platelets (GNP) were fully densified by Spark Plasma Sintering. The effect of GNP on the electrical performance of the composites was analyzed by impedance spectroscopy as a function of temperature (150 – 800 °C) and oxygen partial pressure (0.21 – 10⁻²⁰ atm). Results show that below GNP percolation threshold (7.1 vol.%), the electrical behavior is dominated by the matrix oxygen-ion conductivity. Above the threshold, the conductivity is predominantly electronic provided by the GNP network. The total conductivity of composites was used as an indicator of GNP stability in different atmospheres. YSZ/GNP

* Corresponding author. E-mail: danielmarinha@gmail.com

composites remain stable in inert conditions up to 600 °C, and in reducing conditions up to 800 °C, making them good alternatives to perovskite-based materials used for electrochemical applications.

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1. Introduction

Graphene-based structures such as graphene nano-platelets (GNP) and reduced graphene oxide have been employed extensively as fillers in ceramic matrix composites. Often, the goal is to improve mechanical and tribological properties [1,2], but it is also used to increase the conductivity of insulators in electrical circuitry, or to facilitate electrical discharge machining [3]. In fact, an effective dispersion of graphene can increase electrical conductivity by several orders of magnitude in otherwise insulating matrix materials, such as Si₃N₄ [1], Al₂O₃ [4] or SiC [5].

Yttria-stabilized Zirconia (YSZ) is a well-known oxygen-ion conductor, and also an electronic insulator. The ionic conductivity of YSZ originates from the aliovalent cationic substitution of Zr⁴⁺ by Y³⁺, which is electrostatically compensated by the creation of oxygen vacancies, as expressed below in Kröger-Vink notation.

The doubly charged oxygen vacancies are mobile, and can diffuse within the material by switching positions with neighbouring oxygen atoms, via a hopping mechanism. The composition containing 8 mol% Yttria is preferred for solid-state electrochemical applications, due to a good combination of cost and electrical conductivity and chemical and mechanical stability in a wide range of temperature and atmosphere composition [6]. Due to its inability to transport electronic current, YSZ is regarded as a pure ionic conductor. However, some materials are mixed ionic and electronic conductor (MIEC). Examples can be found in perovskite-based materials, with general ABO₃ crystalline structure, where the B site is

occupied by transition metals that can switch between oxidation states, so electrons can flow along neighbouring atoms. The consequent changes in oxidation states in the lattice are electrostatically compensated by oxygen vacancies, which then give rise to oxygen-ion conductivity. These perovskites [7] are commonly used as solid oxide fuel cell and electrolyser components [8], oxygen transport membranes [9], and electro-catalytic supports [10]. In these applications, the materials are submitted to high temperatures (600–900 °C), and exposed to wide oxygen partial pressure gradients ($1 - 10^{-29}$ atm) and reactive atmospheres. There is an intrinsic trade-off between chemical stability and electrochemical performance [11], and a reasonable compromise has been particularly challenging to obtain with MIEC perovskites [12–14].

In this context, the possibility of combining the high electronic conductivity of graphene with the stability and ionic conductivity of 8YSZ in the form of a composite is an interesting alternative for high temperature applications. The room temperature conductivity of YSZ/reduced graphene oxide composites reportedly varies between 1.1×10^{-1} and 1.2×10^2 S·cm⁻¹ [16,17]. To the best of our knowledge, the only results reported as a function of temperature mention an increase from 19 to 22 S·cm⁻¹ between room temperature and 500 °C, respectively [18,19], in 8 mol% Yttria-doped Zirconia. However, these studies do not mention the interaction between oxygen-ion conduction and graphene, nor on the stability of such composites, particularly at high temperature and different atmospheric compositions, which are critical aspects from an electrochemical application perspective.

Therefore, the objectives of the present work are to characterize the mixed ionic and electronic conductivity, and the stability, of fully dense YSZ/GNP composites, as a function of temperature and oxygen partial pressure.

2. Materials and methods

YSZ/GNP composites containing 0, 2.5, 3.75, and 5.0 wt.% of GNP (type N006, Angstrom Materials Inc., USA with nominal thickness and x-y dimensions of 10-20 nm and 14 μm, respectively) were prepared.

GNP were first dispersed in isopropyl alcohol by sonicating the suspension for 1 h in an ultrasonic bath. In parallel, another isopropyl alcohol suspension containing YSZ powders (TZ-8YS, Tosoh Co., Japan) was attrition milled for 30 min, using YSZ grinding media. Afterwards, the GNP-based dispersion and the YSZ slurry were blended together for 1 h, using a paddle blade mixer in conjunction with a sonication bath. Solvent was evaporated in a rotary-evaporator at 95 °C, dried at 120 °C and sieved through a 63 µm mesh. The GNP volume content (vol.%) was estimated considering density values of 6.0 g.cm⁻³ for YSZ [20] and 2.0 g.cm⁻³ for GNP. Therefore, the composites with 2.5, 3.75, and 5.0 wt.% of GNP contained 7.1, 10.5, and 13.6 vol.% GNP, respectively, and were labelled as “7GNP”, “10GNP”, “14GNP” (Table 1), and sample with 0 vol.% GNP was labelled as “YSZ”.

Bulk samples were spark plasma sintered (SPS, SPS-510CE, Fuji Electronic Industrial Co., Ltd., Japan) into disc specimens of 20 mm diameter and 2.2 mm height applying 50 MPa of uniaxial pressure, using a vacuum atmosphere of 6 Pa, and maximum temperatures of 1310 °C (YSZ) and 1350 °C (YSZ/GNP composites) for 7 min. The apparent densities were determined by Archimedes’ method in distilled water, the theoretical density, ρ_{th} , of the composites being 5.71 (7GNP), 5.58 (10GNP), and 5.49 (14GNP) g.cm⁻³.

The microstructural characterization was carried out by confocal micro-Raman spectroscopy (Alpha300 WITec GmbH, Germany), X-ray diffractometry (XRD, Bruker D5000, Siemens, Germany) and field emission scanning electron microscopy (FESEM, S-4700, Hitachi, Japan). Raman maps of 30 × 30 pixels, recording one spectrum per pixel and using 1 s of acquisition time, were acquired on 30 × 30 µm² scanned areas using a laser wavelength excitation of 532 nm. XRD patterns were collected in step-scanning mode with Cu-K α radiation in a range of detection of 10° < 2 θ < 80°, with a scanning rate of 2°·min⁻¹ in steps of 0.05°. The specimens were observed by FESEM on fracture cross-sectioned surfaces, and on polished top surfaces after thermally etching, in air, at 1250 °C for 30 min. Median grain diameter, d_{50} , and aspect ratio, AR_{50} , of the YSZ matrix were quantified by imaging analysis methods on SEM images considering at least 200 features.

Electrochemical impedance spectra were recorded (Model 7260, AMEL Instruments) between 155 to 630 °C using 50 °C steps, using a signal amplitude of 100 mV and frequency sweep between 1 MHz and 0.1 Hz. Pellet surfaces were polished and sputtered with Pt to serve as electrodes. During electrical measurements the atmospheric oxygen partial pressure, p_{O_2} , was changed between 10^{-20} , 10^{-5} , and 0.21 atm, by flowing 3% H_2 (balanced in He), Ar and N_2/O_2 (reconstituted air), respectively. The flow rate was fixed at of 2 L.h⁻¹ using a mass-flow controller (EL-flow, Bronkhorst, France). The p_{O_2} was measured exiting the sample chamber using a commercially available oxygen pump-gauge (Gen'Air, SETNAG, France). The impedance spectra were modelled in ZView® software using an equivalent circuit (Figure 1), consisting of a series of resistances, R , in parallel with constant phase elements, CPE [21,22]. The impedance of a CPE element is given by $Z = (Q(i\omega)^n)^{-1}$ where Q and n are the fitting parameters and ω the angular frequency, with the related capacitance $C = (R^{1-n}Q)^{1/n}$.

Figure 1 – Equivalent circuit consisting of a series of parallel arrangements of resistances, R_i , and CPE elements, used to fit the impedance spectra. HF, MF and LF correspond to high, medium and low frequency ranges, respectively.

4-electrode measurements were made in bar $2 \times 2 \times 10$ mm samples cut at widest section of the pellets. The electrical conductivity, σ , was calculated from the resistance, R , and sample geometric factor (ratio between sample cross sectional area, A , and inter-electrode thickness, h , according to $\sigma = \frac{1}{R} \cdot \frac{A}{h}$). Activation energy, E_a , was calculated from the slope of linear regression fits of Arrhenius conductivity plots. For simplicity reasons the conductivity is discussed based on values at a reference temperature of 300 °C.

3. Results

3.1 Structural Characterization

Table 1. Main morphological characteristics of composites: relative density, ρ ; median particle size, d_{50} , and aspect ratio, AR_{50} ; Raman I_D/I_G values for the composites. (*) The I_D/I_G value for pristine GNP is 0.12.

Sample	GNP content (vol.%)	ρ (%TD)	d_{50} (μm)	AR_{50}	I_D/I_G^*
YSZ	0	99.9	0.8	1.4	---
7GNP	7.1	99.8	1.0	1.4	0.15
10GNP	10.5	99.1	0.8	1.4	0.14
14GNP	13.6	99.2	0.9	1.4	0.16

SEM images of the surface of YSZ/GNP composites show homogeneous microstructures (Figure 2), with nearly equiaxed grains, with d_{50} values between 0.8 – 1.0 μm , and identical aspect ratio (Table 1). Porosity was practically absent from the YSZ sample, and very few pores were visible at triple points in the YSZ/GNP composites, which is consistent with the relative density values > 99 %TD. Cross-section micrographs show GNP are located at the YSZ grain boundaries, and are well dispersed in the matrix even at higher loads (Figure 3). Further, the GNP are preferentially oriented along their ab planes, leading to an anisotropic microstructure.

Figure 2. SEM micrographs of the thermally etched surfaces of YSZ (a) and composites 7GNP (b), 10GNP (c) and 14GNP (d).

Figure 3 – SEM micrographs of the fracture surfaces of the GNP composites: 7GNP (a), 10GNP (b), 14GNP (c) and higher magnification image of GNP in 10GNP (d).

The micro-Raman spectra of the sintered samples and pristine GNP were compared (Figure 4a). All spectra show the three main characteristic Raman bands of GNP: D- ($\sim 1360 \text{ cm}^{-1}$), G- ($\sim 1590 \text{ cm}^{-1}$), and

2D- ($\sim 2717 \text{ cm}^{-1}$). The intensity ratio between D-and G-bands (I_D/I_G) is a parameter often used to evaluate the quality of GNP, being higher for more defective GNP. All composites exhibit low ratios, only slightly higher than the value obtained for pristine GNP (Table 1). XRD patterns correspond to the cubic phase of YSZ, with the additional graphene diffraction peaks appearing at higher GNP content (Figure 4).

Figure 4. a) Average micro-Raman spectra of the pristine GNP, and YSZ/GNP composites showing the characteristic D-, G-, and 2D-bands of graphitic materials and b) XRD patterns of the composites as a function of the GNP content.

3.2 Electrical characterization

Impedance measurements were performed as a function of temperature under 3% H_2 atmosphere to provide an extremely reducing environment ($p_{\text{O}_2} \sim 10^{-20} \text{ atm}$) and avoid oxidation of the GNP. Impedance spectra show a marked difference between composites with $\text{GNP} < 7.1 \text{ vol.}\%$ and $\text{GNP} > 7.1 \text{ vol.}\%$ (Figure 5).

The impedance spectra of YSZ and 7GNP (Figure 5a) display three features at high (HF), medium (MF) and low frequencies (LF), characteristic of oxygen ion conductors [21,22]. The LF response, with a relatively high capacitance of $\sim 10^{-4} \text{ F.cm}^{-1}$, was attributed to the oxygen exchange reaction at the platinum electrodes. This feature is irrelevant for the purposes of this work, and we will henceforth focus on the

sample response. The capacitance of the HF ($\sim 10^{-12}$ F.cm⁻¹) and the MF ($\sim 10^{-9}$ F.cm⁻¹) features of the YSZ sample did not change with temperature (not shown here). Values and behavior are consistent with the bulk and grain boundaries responses for YSZ [6], and were therefore assigned correspondingly. Compared to the YSZ, the MF feature of 7GNP is much larger, indicating that the grain boundary response is significantly affected by the presence of graphene.

In contrast, impedance spectra of 10GNP and 14GNP composites (Figure 5b) are dominated by a single inductive response in the 4th quadrant, which is typical of samples whose impedance is of the same order of magnitude as the impedance of cabling and wiring of the setup [23]. The total sample conductivity can still be determined, but it is not possible to deconvolute the bulk and grain boundary responses in these samples.

Figure 5 – Impedance spectra at 259 °C in reducing atmosphere for: a) YSZ and 7GNP composite (magnified on inset) and b) 10GNP and 14GNP composites.

Electrical conductivity plots versus temperature also show a different behavior between samples below and above 7.1 vol.% GNP (Figure 6). Comparing YSZ and 7GNP samples shows that the total conductivity decreases with the addition of 7.1 vol.% GNP, but then increases significantly with further increase to 10.5 vol.% and 13.6 vol.%. At 300 °C, the conductivity of 10GNP ($3.1 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$) is over 4 orders of magnitude higher than for YSZ, reaching the maximum values for 14GNP ($7.8 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$). Moreover, the Arrhenius conductivity plots (Figure 6b) show that the composites with GNP content below 7.1 vol.% have higher activation energies (1.1 eV) than composites with higher GNP content (0.1 eV).

a)

Figure 6 –Total electrical conductivity of samples at 300 °C as a function of GNP vol.% (a); Arrhenius plot of the total electrical conductivity of samples (b).

The electrical conductivity of 10GNP was also measured in 4-electrode configuration, in the direction parallel to the alignment of the GNP. Results were compared with impedance spectroscopy results, which instead measures conductivity perpendicularly to the GNP alignment (Figure 7). The electrical conductivity is 1.7 times higher when measured in 4-electrode configuration.

Figure 7 –Total electrical conductivity sample 10GNP composite measured by impedance spectroscopy (open symbols) and 4-electrode setups (full symbols).

3.3 Oxidation stability

The oxidation stability of the composites was tested by measuring the impedance at different p_{O_2} (Figure 8). Here we show the results for 10GNP measured for 24 h at 800 °C in H_2 ($p_{O_2} \sim 10^{-20}$ atm) and 7GNP measured for 7 days at 600 °C in Argon ($p_{O_2} \sim 10^{-5}$ atm) (Figure 8a and 8b, respectively). The variation of the total sample conductivity, σ , relative to initial conductivity, σ_0 , is below 2% for the duration of the tests. These results were reproducible for all composites.

Figure 8 – Impedance spectra under H₂ in isothermal conditions of 10GNP at 800 °C for 24 h (a) and 7GNP at 600 °C for 72 h (b); Corresponding variation of total conductivity, σ , relative to initial conductivity, σ_0 , of the composites (c).

However, when exposed to air ($p_{O_2} = 0.21$ atm) at 600 °C, the impedance response of the composites increases rapidly with time. The impedance of sample 14GNP evolves from an inductive to a capacitive type response, as marked by a gradual shift from the 4th to the 1st quadrant of the Nyquist plots, in less than 7 hours (Figure 9a) . During the 13 h of the test, the electrical conductivity decreases almost 65 times relative to the initial values. Post-mortem SEM observations of the composites show platelet-shaped voids aligned in the microstructure (Figure 9b).

a)

b)

Figure 9 – Impedance plots of 14GNP in isothermal conditions during 13 h at 600 °C in air, recorded at 1 h intervals (a); Post-mortem SEM micrograph of the fractured cross-section (b).

4. Discussion

In this study we characterized the electrical conductivity of YSZ/GNP composites and their oxidation stability, based on impedance spectroscopy measurements. This technique allows differentiating between the electrical responses of the bulk and from the grain boundaries [6], and their relative contribution to the overall electrical behavior of the composites. While the bulk conductivity intrinsically depends on the chemical composition, the grain boundary conductivity depends both on the local chemistry of the grain-to-grain interfaces, but also on the density of grain boundaries: it increases when the average grain size increases (lower grain boundary density). In summary, the matrix and the GNP network in the composites must remain chemically and structurally stable during processing, and must have similar microstructures after sintering. In these conditions, the electrical properties can be directly compared and the potential effects of GNP can be analyzed.

4.1 Structural results

YSZ/GNP composites were sintered using SPS to avoid the hindering effect that secondary phases have on densification, and which often result in increased residual porosity and finer microstructures with increasing GNP concentration [5]. The SEM images (Figure 2) show that the SPS thermal cycles were

successful in reaching full sample densification, while maintaining similar average grain size and morphology of the microstructures. Further, a good GNP dispersion along the YSZ grain boundaries (Figure 3) ensures that any effect they have on electrical properties is limited to the grain boundaries, and should be visible at the corresponding frequency ranges of the impedance spectra.

The reducing environment during SPS may protect against GNP oxidation, but may also result in partial reduction of the matrix, and in the case of YSZ, potentially form zirconium carbide [24]. However, XRD patterns of YSZ and composites in this study show sharp, symmetrical peaks, corresponding to 8 mol% Ytria-doped Zirconia (Figure 4b). In addition to GNP diffraction peaks for 10GNP and 14GNP, no other secondary phases were detected. We conclude that the amount of secondary phases either remained below the detection threshold, or are totally absent. Therefore, the electrical behavior of the matrix is expected to correspond to the well-known behavior of YSZ.

The chemical and structural integrity of the GNP was verified by Raman spectroscopy. The Raman positions reported for the D, G and 2D graphene peaks vary slightly across the literature. This variation is associated with the presence of defects, residual stresses, and surface chemistry of the graphene, as well as with possible interaction with the matrix material [24–26]. A detailed discussion of these effects is out of the scope of this work. Suffices to say that the Raman signature of the composites, as well as the I_D/I_G parameter, matches well to that of pristine GNP (Figure 4a and Table 1). This indicates that SPS processing does not significantly introduce additional defects to the GNP, and that the degree of agglomeration of GNP in the composites does not change with GNP content. Contrarily to some reports, we observed no thinning effect due to SPS processing [27].

In summary, these results show that YSZ/GNP composites are structurally similar and therefore, that the electrical behavior can be independently analyzed as a function of the GNP content.

4.2 Electrical characterization

The electrical properties are significantly affected by the presence and the quantity of GNP in the composites. The sharp increase in total conductivity observed between 7.1 and 10 vol.% GNP, combined with the decrease in activation energy (Figure 6b), are clear indications that the GNP network reaches the percolation threshold just above 7.1 vol.%.

Samples YSZ and 7GNP, below the percolation threshold, the electrical behavior is clearly dominated by the oxygen-ion conductivity provided by the YSZ matrix, as evidenced by the capacitive responses of the bulk and grain boundaries observed in corresponding impedance spectra (Figure 5a). Moreover, the activation energy is indicative of the nature of the charge carrier and conduction mechanism. Both YSZ and 7GNP samples have $E_a = 1.1$ eV (Figure 6b), which is typical of oxygen-ion conduction via vacancy hopping in YSZ in the range of 200 – 700 °C [28]. From Figure 5a, it is possible to see that the specific bulk conductivity of YSZ is about 10% higher than in 7GNP. The bulk conductivity is an intrinsic property of the material, and therefore, it is independent of the microstructural features of a polycrystalline material. However, small differences can be expected whenever a secondary phase is blocking to the main charge carriers [29]. Moreover, this increase is observed at frequency ranges associated with grain boundaries interfaces [30]. As previously discussed, this is in agreement with the presence of GNP at the grain boundaries (Figure 3), and indicates that the GNP are blocking to oxygen-ion diffusion between YSZ grains.

The electrical conductivity of samples 10GNP and 14GNP are four orders of magnitude higher than the oxygen-ion conductivity of YSZ and 7GNP at 300 °C. Electrons have much higher mobility than oxygen ions, and large conductivity increases are expected, even at low charge carrier concentrations [31,32]. These observations are in agreement with the formation of an electronically conducting GNP network percolating the matrix. Since the electrical conductivity follows an Arrhenius behavior, the conductivity values can be extrapolated to room temperature, where the difference increases up to 11 orders of

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4 magnitude, which is relevant for electrical discharge machining. It is interesting to note that the
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6 conductivity of the composites above the percolation limit still increases with increasing GNP content.
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8 This is likely an approximation error, since the conductivity calculation does not take into account the
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10 GNP volume fraction, but the geometry of the composite.
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14 In conventional perovskite mixed ionic and electronic conductors, the electronic conduction mechanism
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16 occurs through small polaron hopping, with typical activation energy that can vary between 0.1 and 0.4
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18 eV [33–35]. The electrical conductivity of composites in this study is closer to the lower limit (Figure 6),
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20 and is consistent with conductivity data reported for YSZ/GNP composites tested in similar temperature
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22 ranges (calculations based on published data [19]).
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26 Conductivity measured in 4-electrode geometry is higher than that obtained by impedance (Figure 7).
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28 This electrical anisotropy is a result of the preferential alignment of GNP (Figure 2) perpendicularly to the
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30 SPS axial pressure during sintering. The anisotropy ratio of conductivity parallel and perpendicular to the
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32 GNP alignment is ~10, which is typical for ceramic/graphene-based composites [5]. Electrical anisotropy
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34 can be tailored near the percolation threshold to obtain a preferential direction for oxygen ion flow that is
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36 perpendicular to that of the electronic current, as in the case of ceramic oxygen transport membranes
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38 whenever the oxygen flux is limited by electronic conductivity [36].
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45 4.3 Oxidation Stability

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48 The stability of high-temperature solid-state ionic materials is notoriously insufficient, and often the most
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50 critical selection criterion of any material used for high-temperature electrochemical applications [37]. In
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52 other domains, ceramic matrix composites are often prone to embrittlement due to oxidation of the
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54 reinforcing carbon fibers, due to oxygen gas diffusion through cracks in the matrix and consequent
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56 oxidation of the fibers [38]. It was unclear how oxygen-ion diffusion would affect the stability of the GNP
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58 network, and its impact on the electrical properties. In this context, it is important to establish the stability
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of YSZ/GNP composites under different conditions of temperature and oxygen partial pressure, and also to oxygen-ion diffusion within the matrix.

The p_{O_2} used during these tests is not sufficiently low to reduce YSZ, and the temperature is well below the SPS sintering temperature, so we assumed that the YSZ matrix was chemically and microstructurally stable during tests. It follows that any evolution of the electrical behavior of the composites *necessarily* indicates changes occurring to the GNP network, regardless of the exact GNP content in that particular sample. This allows direct comparison of the composite stability across samples.

In air and at 600 °C, the electrical conductivity of the 14GNP composite quickly decreases with time (Figure 9a), and after 13 h its impedance spectra is similar to that of YSZ. This behavior is consistent with a change in the major charge carrier controlling the conductivity response, from electrons to oxygen-ions. Consequently, GNP in the composites are sensitive to atmospheric oxygen, most likely oxidizing and burning off, which explains voids in post-mortem micrographs (Figure 9b).

However, impedance recorded at lower $p_{O_2} < 10^{-5}$ atm shows that GNP in the composites is stable at 600 °C in Argon and at up to 800 °C in H₂. This is a remarkably stable behavior, considering that oxygen-ion conductivity remains constant within experimental conditions [39], meaning that there is significant oxygen ion diffusion within the lattice. Consequently, we conclude that the GNP are not oxidized by oxygen ion species, at that somehow the reducing atmosphere avoids their oxidation. We further conclude that YSZ/GNP composites can be used in conditions that are typical of high-temperature electrochemical device ($p_{O_2} < 10^{-5}$ atm, and $T < 800$ °C) without significant degradation. This is particularly relevant since the stability of perovskite-based mixed ionic and electronic conductors is particularly diminished in reducing conditions, causing phase segregation and de-mixing, as well as changes to the thermal expansion coefficient [40,41]. With this in mind, it would be interesting YSZ/Graphene composites seem particularly promising as oxygen transport membranes, in presence of an oxygen partial pressure gradient and a cross-flow of ionic and electronic charge carriers, where GNP could be aligned to improve

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4 electronic conductivity in the oxygen flux direction [36], while minimizing the ion-blocking effects.
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6 Secondly, as an alternative to perovskite-based SOFC interconnects, thus avoiding the use of chromites
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8 [42], and again taking advantage of electrical anisotropy, this time to minimize oxygen ion conductivity
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10 and maximize electronic conductivity.
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13 14 **5. Conclusions**

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17 Electronic conductivity can be introduced in YSZ bulk materials, by adding small amounts of well-
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19 dispersed GNP. The GNP network reaches percolation at 7.1 vol.% GNP content as indicated by an
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21 increase total electrical conductivity of over 4 orders of magnitude at 300 °C. Simultaneously, the
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23 electrical behavior changes from ionic- to electronic-dominated electrical conduction. The ionic
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25 conductivity is hindered by the presence of GNP at the grain boundaries blocking oxygen-ion diffusion.
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27 Above the percolation threshold, YSZ/GNP composites can be effectively considered as extrinsic mixed
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29 ionic and electronic conductors, and remain stable in inert conditions up to 600 °C, and reducing
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31 conditions up to 800 °C. YSZ/GNP composites are considered good candidates for high-temperature
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33 electrochemical applications, where conventional perovskite-based alternatives have well-known stability
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35 issues.
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Table 1. Main morphological composite characteristics: relative density, ρ ; median particle size, d_{50} , and aspect ratio, AR_{50} ; Raman ID/IG values for the composites. (*) The ID/IG value for pristine GNP is 0.12.

Sample	GNP content (vol.%)	ρ (%TD)	d_{50} (μm)	AR_{50}	I_D/I_G^*
YSZ	0	99.9	0.8	1.4	---
7GNP	7.1	99.8	1.0	1.4	0.15
10GNP	10.5	99.1	0.8	1.4	0.14
14GNP	13.6	99.2	0.9	1.4	0.16

Figure 1
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Figure 2

Figure 1. SEM micrographs of the thermally etched surfaces of YSZ (a) and composites 7GNP (b), 10GNP (c) and 14GNP (d).

Figure 3

Figure 1 – SEM micrographs of the fracture surfaces of the GNP composites: 7GNP (a), 10GNP (b), 14GNP (c) and higher magnification image of GNP in 10GNP (d).

Figure 4

Figure 1. a) Average micro-Raman spectra of the pristine GNP, and GNP in composites showing the characteristic D-, G-, and 2D-bands of graphitic materials and b) XRD patterns of the composites as a function of the GNP content.

Figure 5

Figure 1 – a) Impedance spectra at 259 °C in reducing atmosphere for (a) YSZ and 7GNP (high frequency range is magnified in top inset, including the bulk response frequency), and (b) and 10GNP and 14GNP composites.

Figure 6

Figure 1 –Total electrical conductivity of samples at $300\text{ }^{\circ}\text{C}$ as a function of GNP vol.% (a); Arrhenius plot of the total electrical conductivity of samples (b).

Figure 7

Figure 1 –Total electrical conductivity sample 10GNP measured by impedance spectroscopy (open) and 4-electrode setups (full).

Figure 8

Figure 1 –Impedance spectra in isothermal conditions of 10GNP under H₂ at 800 °C for 24 h (a) and 7GNP at 600 °C for 72 h (b); Corresponding variation of total conductivity, σ , relative to initial conductivity, σ_0 , of the composites.

Figure 9

Figure 1 – Impedance plots of 14GNP in isothermal conditions during 13 hours at 600 °C in Air, recorded at 1 hour intervals (a); Post-mortem SEM micrograph of the fracture cross-section (b).