

Special Issue on Cellular Materials

Biomimetic cork-based CeO₂ ecoceramics for hydrogen generation using concentrated solar energy

R.C. Pullar^{a*}, L. Gil^b, F.A.C. Oliveira^c

^aDepartamento de Engenharia de Materiais e Cerâmica, CICECO, Universidade de Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

^bDGEG - Direção Geral de Energia e Geologia, Divisão de Estudos Investigação e Renováveis, Av. 5 de Outubro 208, 1069-203 Lisboa, Portugal

^cLNEG - Laboratório Nacional de Energia e Geologia I.P., Unidade de Energia Solar, Estrada do Paço do Lumiar 22, 1649-038 Lisboa, Portugal

Abstract

Naturally occurring and sustainable materials can be used as a template to create biomimetic/biomorphic ceramics, known as Ecoceramics (environmentally conscious ceramics). In this work, cork was chosen as template to produce novel ceria (CeO₂) ecoceramics, for applications in water splitting for H₂ production via direct concentrated solar thermochemical fuel production (TCFP). The cork powder was pyrolysed at 900 °C and the resulting carbon skeleton was infiltrated with an aqueous CeO₂ precursor, and then heated at 1000 °C for 2 h to produce the ecoceramic. The cellular structure of the cork was maintained, with hexagonal cell dimensions of 20–30 μm in diameter, but the grains were nanoscale at ≤100 nm. XRD data confirmed that CeO₂ was the only crystalline phase obtained. An important feature was that, while the rectangular side walls were maintained to hold the three-dimensionally ordered macroporous (3DOM) cellular cork structure, the rear hexagonal walls were pierced repeatedly through the structure, unlike in the original cork structure, which will allow gasses such as H₂ to permeate well into the structure, greatly increasing the reactive area available for catalysis. The next step will be to test the capabilities of both the regular, porous 3DOM structure and the nanoscale grains for thermochemical water splitting to produce hydrogen under direct concentrated solar energy. © 2016 Portuguese Society of Materials (SPM). Published by Elsevier España, S.L.U. All rights reserved.

Keywords: cork; ecoceramics; ceria; concentrated solar energy.

1. Introduction

Cellular ceramics constitute a specific class of materials consisting of a three-dimensional assembly of pores possessing a specific shape leading to a solid with a high level of porosity (greater than 70 vol. %). The basic unit structure of cork is termed ‘cell’; that is, an enclosed empty space possessing faces and solid edges. The faces can either be fully solid or void, giving rise to either a closed cell or an open-cell material, respectively.

In the tangential section, cork cells are polygons

(mostly six sided hexagons), arranged in a honeycomb-type structure. The radial and transversal sections of cork resemble a brick wall, with the rectangular cells aligned in parallel rows. In these two sections, cell walls show undulation in raw cork, although this corrugation can be lowered in processed (boiled) cork. An ideal average cell has a prism height of 40 μm, a base edge of 20 μm and a wall thickness of 1 μm but large variations can be observed [1,2].

Closed cell materials are suitable for acoustic and heat insulation and lightweight structures, whereas open cell ones are widely used in applications involving

* Corresponding author

E-mail address: rpullar@ua.pt (R.C. Pullar)

fluid transport such as molten metal filtration, catalytic substrates, radiant burners, solar radiation volumetric absorbers, and heat exchangers, among others. In particular, open-cell ceria-based foams are being envisaged for solar thermal hydrogen production, which is based on a two-step process leading to water splitting [3]. Such an H₂ production path ought to present higher efficiencies than electrolysis. This still remains to be fully proven, however.

Ceria-based materials are known for their capability of achieving remarkably high vacancy concentrations at elevated temperatures and low oxygen partial pressures [4]. Hence, these materials are attractive as reactive intermediates in thermochemical redox cycles for the production of solar fuels [5]. These H₂O/CO₂-splitting cycles consist of two separate thermo-chemical reactions, namely, a high-temperature (endothermic) reduction and a low-temperature (exothermic) oxidation. Reduction proceeds through the formation of oxygen vacancies and the release of gaseous O₂, resulting in a stoichiometry change, δ . Oxidation proceeds with H₂O and/or CO₂, thereby releasing H₂ and/or CO and reincorporating oxygen into the lattice. Thus, the number of oxygen vacancies created during reduction is directly related to the yield of fuel production that can be achieved. Pure ceria is expected to achieve a maximum solar-to-fuel energy conversion efficiency for the production of H₂ of ~20% at 1000 K oxidation temperature [6]. This is typically achieved providing that the reduction reaction takes place at T = 1800 K and PO₂ = 1 Pa (10⁻⁵ atm). In such a case, experimental data shows the oxygen non-stoichiometry of undoped ceria can be as large as 0.1 [7].

Comprehensive reviews on solar thermo-chemical processing have been carried out by Fletcher [8] and Steinfeld [9]. In thermochemical fuel production, concentrated solar energy provides the high-temperature process heat to drive endothermic reaction cycles [10]. More recently, it has been shown that reaction kinetics can be enhanced using 3DOM CeO₂. Indeed, Rudisill *et al.* [11] studied the influence of pore structure on the overall process efficiency and reaction kinetics of CO₂ splitting by full thermochemical cycling with CeO₂, i.e. thermal rather than chemical reduction and subsequent fuel production. 3DOM CeO₂ templates were reduced at ~1200 °C in N₂, and the reduced CeO_{2,δ} materials were deoxidised under CO₂ at ~850°C. 3DOM CeO₂ provided a 10-fold enhancement in CO production rate when compared to nonporous CeO₂ under similar conditions. Such a boost in reaction kinetics allowed for extremely rapid cycling, with less than a minute required for complete

reduction or oxidation. The purpose of this study is therefore to develop 3DOM CeO₂ from cork templates. This study has some significance, because the interconnected pore network of cork, and even the cork cell walls plasmodesmata, could provide the means to improve the high-temperature redox properties of CeO₂, in the particular case of H₂ production by a non-conventional route. Such possibility is regarded with great interest for practical thermochemical reactor systems, as it would allow fuel production at lower temperatures by enabling faster cycling. Rapid cycling rates are important for increasing the throughput of fuel over a given time.

Cork is the bark of a slow-growing oak (*Quercus suber* L.), found only in a few regions. Europe supplies 85% of all cork, and Portugal is the major global producer (50%) [12]. Cork is an exceptionally sustainable and renewable resource, as the bark is harvested every 9–13 years without harming the tree, which continues to live on as a carbon sink for up to 300 years [13]. Cork forests are one of the best global examples of balanced conservation and development, playing a key role in ecological processes (water retention, soil conservation, carbon storage). Furthermore, cork oak trees store more carbon in order to regenerate the lost bark, so a harvested cork tree absorbs up to five times more CO₂ than a virgin one [14]. Cork sequesters up to 5.7 T CO₂/ha/yr, and the 2.3M ha of cork forests worldwide sequester 14.4M T CO₂/yr [15]. In this way, any CO₂ released from the pyrolysis of the cork templates will be offset by the growth of new bark on existing trees. Portugal's cork oak forests are also considered to be "Europe's Amazon forest", supporting the greatest bio-diversity anywhere in Europe [14]. A review on cork as a green and sustainable material can be found elsewhere [16]. Attention is drawn to the fact that the cork powder used here is a low cost by-product of the cork industry, being its main waste, and typically 32–37,000 tonnes are produced annually in Portugal, and ~50,000 tonnes globally [17]. Although this data is not recent, there is no new information on cork powder quantities. Nowadays, less cork is produced and processed, but more cork products based on ground cork are manufactured and thence it is estimated that the overall cork powder quantity remains unchanged. Therefore, there is also an element of wastes valorisation in this work. Clearly, the use of such a sustainable material for renewable energy applications would be ideal.

The cellular structure of wood can be impregnated by a fluid, and transformed into an inorganic replica of the original structure, to create a biomimetic material [18].

The wood is first pyrolysed to a pure carbon skeleton, maintaining its structure but becoming highly nanoporous, so it can be impregnated with a solution, which converts to the inorganic phase on heating in air with loss of the carbon. This can be used as a template for the synthesis of novel inorganic materials with highly anisotropic cellular microstructures, a new class of ceramics now referred to as *Ecoceramics* (Environmentally conscious ceramics) [19].

A wide range of biomimetic materials have been created, maintaining the structure of the wood as novel forms of carbides, oxide ceramics and composites, with tailored chemical, physical and mechanical properties [20]. The first biomorphic ceramics produced were of “SiC wood” [21] from charcoal, and since 1998 several types of pyrolysed wood were used as templates to create SiC “ceramic wood” [22,23], as well as oxide ceramics such as CeO₂ [24,25]. Many different soft and hard woods have been used as pyrolysed templates for Ecoceramics, but cork was never used, despite its obvious suitability, until the pioneering work by Pullar *et al.* [26], although this use was previously referred to as a possible future trend [12]. Pullar *et al.* created the first ever cork-based Ecoceramics, in the form of magnetic hexagonal ferrite ceramic foams, with the cellular structure of cork. In this paper we report the first ever synthesis of cork-based CeO₂ ecoceramics.

2. Experimental

2.1. Synthesis

Cork powder supplied by Amorim (resulting typically from the processing, trimming and shaping of cork stoppers for wine), was coarse by the standards of the industry (it is typically <250 μm), with particle sizes between 250 and 500 μm, but containing typically sized cells of around 20–30 μm in diameter [1]. One of the advantages of using cork for this purpose is the cells shape and arrangement, and also the existing very small channels crossing the cell walls. As-received powder was pyrolysed under argon in a graphite furnace at 900 °C, while contained in alumina crucibles with loose-fitting lids. The heating rate was 5 °C min⁻¹ to 150 °C, then 10 °C min⁻¹ to 900 °C with a dwell time of 30 min, after which the samples were cooled down at a rate of 10 °C min⁻¹.

A solution of cerium nitrate (Ce(NO₃)₂·6H₂O, Aldrich, 99 %) was used to create the ecoceramics. The amount of carbon present was calculated from the weight of the pyrolysed cork to be used, and an aqueous solution was used with the equivalent number of moles of cerium. A

large excess of water was used to dissolve the cerium nitrate. The pyrolysed cork powder was then infiltrated with the solution under vacuum, as the water was removed on a rotary evaporator at 60 °C and 70 mPa pressure. The pyrolysed cork is nanoporous, and readily absorbs a liquid into these pores when under vacuum. The infiltrated cork was then heated in air to 1000 °C at 5 °C min⁻¹ with a dwell time of 2 h at 1000 °C, to form CeO₂, followed by natural cooling. The carbon template skeleton was fully combusted, leaving just a pure ceria ecoceramic.

2.2. Characterisation

Differential Thermal Analysis (DTA) – Thermo-Gravimetric Analysis (TGA) was carried out on a SETARAM Labsys TG-DSC16, under flowing air, up to 1000 °C at a heating rate of 10 °C min⁻¹, using 30–50 mg of material. Scanning Electron Microscopy (SEM) was carried out on a Hitachi S-4100 at 10–20 kV on samples coated with a thin layer of carbon. The crystal structure of the ecoceramic was identified by X-ray diffraction (XRD) using a Rigaku Geigerflex D/max Series diffractometer with Cu Kα radiation.

3. Results and Discussion

The DTA-TGA plots for cork powder and pyrolysed cork powder are compared in Fig. 1. The cork wood (Fig. 1a) loses about 5% weight between 80–120 °C, which is the loss of absorbed moisture. A further 10 wt. % is then lost between 200–300 °C, which is the loss of initial organic products by thermal degradation, followed by a large loss of around 45% weight between 300–400 °C, as the more volatile organic substances and hydrocarbons are lost, with an accompanying exotherm. This is in agreement with results from previous thermogravimetric studies on cork [27]. Then the remaining carbon and hydrocarbons are lost much more gradually between 450–900 °C, an endothermic process with a further weight loss of about 30 %. The remaining material after heating to 1000 °C (<10 wt. %) is ash. The pyrolysed cork (Fig. 1b) loses a similar 10% up to 200 °C, presumed to be adsorbed water, but then the exothermic process seen in the cork wood is missing, unsurprisingly, as the pyrolysis process has already removed any volatile compounds, converting them to carbon. There is a similar gradual weight loss between 400–800 °C, as the carbon skeleton is lost through a highly endothermic process, again leaving <10 wt. % as ash. The DTA-TGA of the ceria precursor infiltrated pyrolysed cork is shown in Fig. 1c).

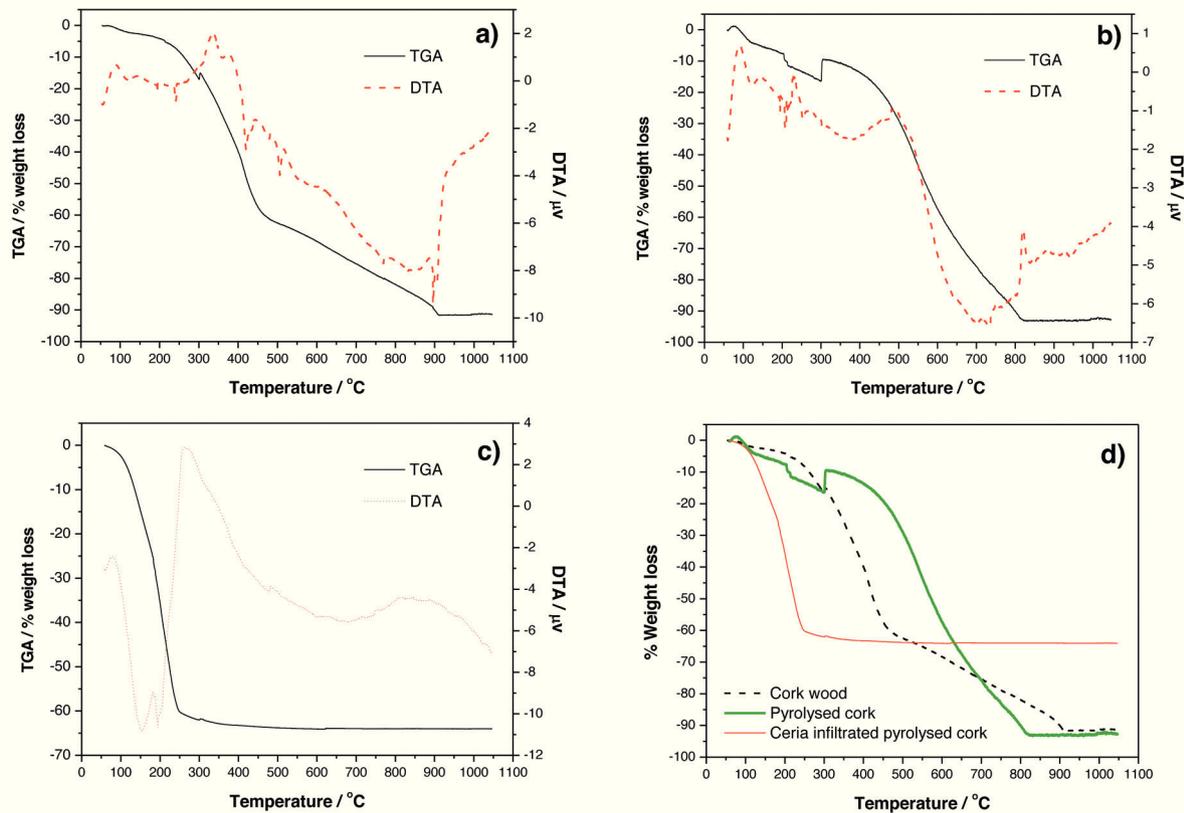


Fig. 1. DTA-TGA plots for a) cork wood powder, b) previously pyrolysed cork powder, c) ceria precursor infiltrated pyrolysed cork powder. The % weight loss of all three is directly compared in d).

It can be seen that there is again an initial endothermic process, but this is followed by a highly exothermic reaction between 200–400 °C, with a weight loss of 60 %. It is known that nitrates are highly combustible at such low temperatures – indeed, they are used as oxidising accelerants to initiate combustion reactions and explosions – and the process is completed by 400 °C, with little subsequent weight loss with further heating. CeO_2 has a mass which is ~40% of that of the salt used, so a 60% weight loss is to be expected, any extra being absorbed water and the carbon template. The DTA peak seen around 850 °C suggests that crystallisation of CeO_2 may be occurring around this temperature, and this will be investigated in future work. The TGA weight loss plots of the three samples are directly compared to the same scale in Fig. 1d), to show the variations in weight loss more clearly.

Judging from the micrographs observed in Fig. 2a), it is evident that the pyrolysed cork has maintained the cork macro- and microstructure, with cell dimensions and cell wall widths being retained. It can also be seen that the Ecoceramics maintained the cellular structure

of the cork after conversion to the ceramic, both on the macroscale (Fig. 2b) and the microscale (Fig. 2c). It should also be noted that these cork-based ecoceramics were much more porous than any previously reported CeO_2 ecoceramics [24,25], which were made from the denser linden wood (*tilia amurensis*) and Eastern white pine (*P. strobus*), respectively. The cell walls had smaller thicknesses than the hexaferrite Ecoceramics reported previously [26], which had 1 μm thick walls made up of large micron scale ferrite grains. The CeO_2 ecoceramics seen here consisted of nanoscale grains ~100 nm, as can be observed in Fig. 2d). Such a small grain size, even after heating to 1000 °C, should enhance their ability as redox based catalysts in energy applications. Another important feature to note is that in many of the cells, while the rectangular side walls are maintained to hold the cork structure, the rear hexagonal/polyhedral walls have a sizeable hole in them, and this feature repeats through the structure. This is a very important difference from the original cork structure, as it will allow gasses such as H_2 to permeate well into the structure, greatly increasing the

reactive area available for catalysis. Cork wood has individually sealed cells, which is why it floats so well and insulates against sound, impact and heat, so this is a useful modification of the cork structure for energy and catalytic applications. This effect was not seen in the hexaferrite cork-based Ecoceramics, which were made from aqueous sol precursors with low nitrate content, and hence it is presumed to be a result of the

rapid and highly exothermic combustion of the nitrate precursors, as discussed above. The XRD pattern of the cork-based CeO_2 ecoceramics fired at $1000\text{ }^\circ\text{C}/2\text{ h}$ is shown in Fig. 3. It can be seen the materials consist of crystalline single phase ceria, analogous to the cubic (hexoctahedral) cerianite phase (F3m3, ICDD 34-394). The next stage will be to evaluate the redox thermochemistry performance of these novel materials.

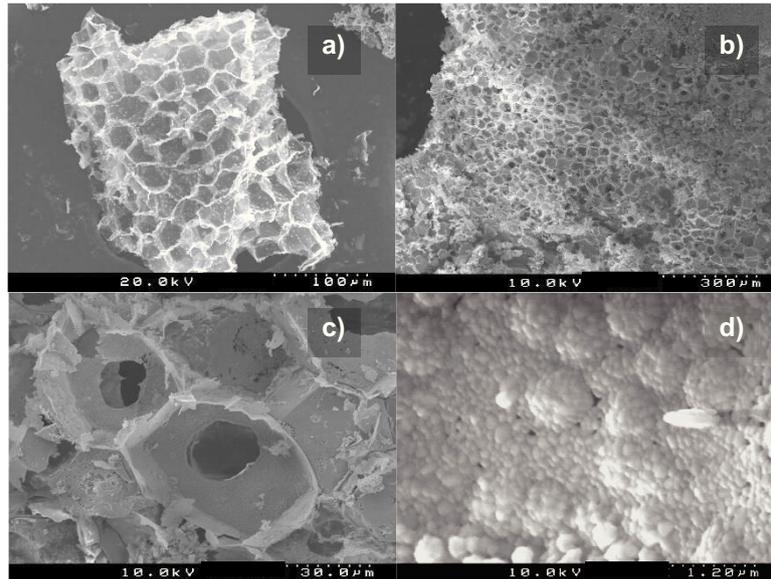


Fig. 2. SEM images of a) cork pyrolysed under Ar at $900\text{ }^\circ\text{C}$, b)-d) pure CeO_2 ecoceramics, after heating at $1000\text{ }^\circ\text{C}$ in air, with the cellular structure of the cork template. Image d) shows the nanoscale nature of the constituent grains of this ecoceramic.

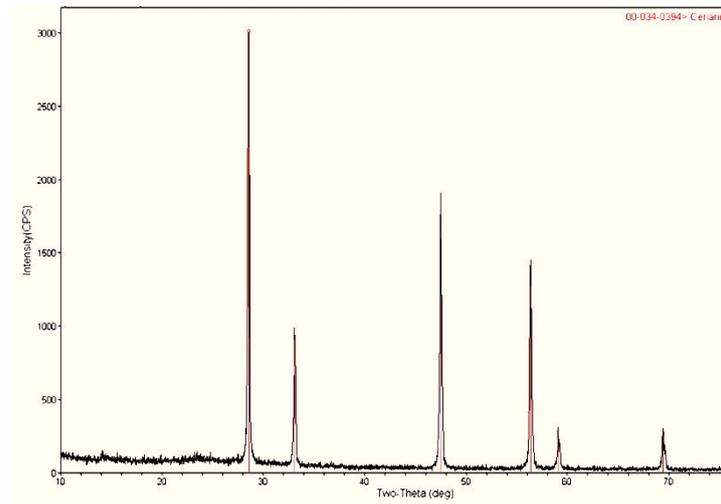


Fig. 3. XRD pattern of the CeO_2 ecoceramics heated to $1000\text{ }^\circ\text{C} / 2\text{ hr}$. The peaks shown are, from left to right, (111), (200), (220), (311) and (400), and the standard used is JCPDF 00-034-0394.

4. Conclusions

Ceria ecoceramics have been successfully made for the first time using cork as a template. The ecoceramics were heated to 1000 °C to produce a pure CeO₂ ceramic, but DTA/TGA data suggests that temperatures of only 850 °C may be sufficient. SEM images showed that the cellular structure of the cork was maintained, with hexagonal cells around 20–30 μm in diameter, and cell walls <1 μm thick. Unlike the large grained hexaferrite ecoceramics made from cork reported previously by Pullar *et al.* [26], the individual grains of these CeO₂ ecoceramics were on the nanoscale size range, being no more than 100 nm in diameter. Another important feature was that, while the rectangular side walls were maintained to hold the cellular cork structure, the rear hexagonal walls were pierced, with these holes repeating through the structure. This is unlike the original cork structure, and will allow gasses such as H₂ to permeate well into the structure, greatly increasing the reactive area available for catalysis. It is envisaged that both the regular 3DOM structure and the nanoscale of the grains will enable these ecoceramics to form enhanced redox catalysts for thermochemical water splitting to produce hydrogen under direct concentrated solar energy. Further work will be devoted to the development of a solar chemical reactor integrating the materials created in the present work, to investigate their performance under solar irradiation conditions.

Acknowledgements

Thanks to Amorim Cork Composites (Portugal) for supplying cork powder. R.C. Pullar wishes to thank the FCT Grant SFRH/BPD/97115/2013 for supporting this work. The authors would like to acknowledge the EU and the seventh framework program for the financial support of this work under the STAGE-STE project with contract number 609837. This work was developed in the scope of the project CICECO–Aveiro Institute of Materials (Ref. FCT UID /CTM /50011/2013), financed by national funds through the FCT/MEC and when applicable co-financed by FEDER under the PT2020 Partnership Agreement.

References

- [1] H. Pereira, *Cork: Biology, Production and Uses*, Elsevier Science, 2007.
- [2] L. Gil, *Cortiça: Produção, Tecnologia e Aplicação* (in Portuguese), INETI, Lisboa, 1998.
- [3] A. Le Gal, S. Abanades, *J. Phys. Chem. C* 116 (2012) 13516.
- [4] M. Mogensen, N.M. Sammes, G.A. Tompsett, *Sol. State Ionics*. 129 (2000) 63.
- [5] S. Abanades, A. Legal, A. Cordier, G. Peraudeau, G. Flamant, A. Julbe, *J. Mater. Sci.* 45 (2010) 4163.
- [6] J.R. Scheffe, A. Steinfeld, *Energy & Fuels* 26 (2012) 1928.
- [7] D. Schneider, M. Godickemeier, L.J. Gauckler, *J. Electroceram.* 1 (1997) 165.
- [8] E.A. Fletcher, *J. Sol. Energy Eng.* 123 (2000) 63.
- [9] A. Steinfeld, *Solar Energy* 78 (2005) 603.
- [10] P. Furler, J.R. Scheffe, A. Steinfeld, *Energy Environ. Sci.* 5 (2012) 6098.
- [11] S.G. Rudisill, L.J. Venstrom, N.D. Petkovich, T. Quan, N. Hein, D.B. Boman, J.H. Davidson, A. Stein, *J. Phys. Chem. C* 117 (2013) 1692.
- [12] S.P. Silva, M.A. Sabino, E.M. Fernandes, V.M. Correló, L.F. Boesel, R.L. Reis, *Int. Mat. Rev.* 50 (2005) 345.
- [13] http://www.corkforest.org/cork_facts.php. – accessed December 2015.
- [14] <http://www.saomarcosdaserra.com/cork.php> – accessed December 2015.
- [15] L. Gil, *Front. Chem.* 2, article 16 (2014).
- [16] A. Mestre, L. Gil, *Cienc. Tecnol. Mater.* 23 (2011) 52.
- [17] L. Gil, *Biomass Bioenergy* 13 (1997) 59.
- [18] J. Martinez-Fernandez, F.M. Valera-Feria, M. Singh, *Scripta Mater.* 43 (2000) 813.
- [19] M. Sing, J. Martinez-Fernandez, A.R. de Arellano-Lopez, *Curr. Op. Solid State Mat. Sci.* 7 (2003) 247.
- [20] H. Sieber, *Mat. Sci. Eng. A* 412 (2005) 43.
- [21] T. Ota, M. Takahashi, T. Hibi, M. Ozawa, S. Suzuki, Y. Hikichi, *J. Amer. Ceram. Soc.* 78 (1995) 3409.
- [22] P. Greil, T. Lifka, A. Kaindl, *J. Eur. Ceram. Soc.* 18 (1998) 1961.
- [23] P. Greil, T. Lifka, A. Kaindl, *J. Eur. Ceram. Soc.* 18 (1998) 1975.
- [24] B. Matovic, S. Boskovic, *Romanian J. Mat.* 38 (2008) 329.
- [25] C.D. Malonzo, *J. Phys. Chem. C* 118 (2014) 26172.
- [26] R.C. Pullar, P. Marques, J. Amaral, J.A. Labrincha, *Mater. Design* 8 (2015) 297.
- [27] M.E. Rosa, M.A. Fortes, *J. Mat. Sci. Lett.* 7 (1988) 1064.