Chemical and thermomechanical compatibility between neodymium manganites and electrolytes based on ceria

V. GIL, J. TARTAJ, AND C. MOURE

Instituto de Cerámica y Vidrio (CSIC), Electroceramics department
C/ Kelsen 5, 28049 Madrid, España

The goal of this work was to study the thermal expansion behaviour and to establish the phase relations between $\text{NdMe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (Me=Ni, Co) solid solutions as cathodes and two electrolytes based on $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$. Doping of electrolyte with 1.0 wt% Bi_2O_3 was employed in order to improve the densification process.

The cathode-electrolyte pairs were obtained by isostatic pressing of constituent powders and posterior sintering using the temperature ranges between 1350–1400 °C for 2 h. The sintering conditions were optimized to obtain highly densified electrolytes and well-developed cathode-electrolyte interfaces.

Scanning electron microscopy observation with EDAX analysis was performed in cathode-electrolyte interfacial regions in order to characterize the obtained microstructures and to determine possible cation diffusions from the cathode into the electrolyte.

It is found that the nickel doped manganite, $\text{NdNi}_{0.5}\text{Mn}_{0.5}\text{O}_3$, is chemically and thermo-mechanically compatible with both electrolytes without formation of new phases up to 1400°C even during long time of treatments.

Keywords: $\text{CeO}_2\text{-Gd}_2\text{O}_3$, manganites, thermal compatibility, chemical compatibility.

Compatibilidad química y termomecánica entre manganitas de neodimio y electrolitos basados en ceria

El propósito del presente trabajo es establecer las relaciones de fase entre soluciones sólidas $\text{NdMe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (Me=Ni, Co) y electrolitos $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ para su uso como cátodos y electrolitos SOFC, respectivamente. El electrolito fue en ocasiones dopado con 1.0 wt% Bi_2O_3 con el objeto de mejorar su densificación. Así mismo se estudia el comportamiento termomecánico de dichos materiales.

Los pares cátodo-electrolito fueron obtenidos a partir de polvos prensados isostáticamente y posteriormente sinterizados utilizando unos rangos de temperatura entre 1350 y 1400°C durante 2h. Las condiciones de sinterización fueron optimizadas para obtener unos electrolitos altamente densificados y unas interfaces cátodo-electrolito bien definidas.

La caracterización microestructural de las regiones interfaciales fue llevada a cabo mediante microscopía electrónica de barrido, además se realizaron análisis EDAX para determinar posibles fenómenos de difusión catiónica desde o hacia el cátodo.

Se puede concluir que la manganita dopada con níquel, $\text{NdNi}_{0.5}\text{Mn}_{0.5}\text{O}_3$, es compatible química y termomecánicamente con los electrolitos basados en ceria, sin formación de nuevas fases incluso después de largos tiempos de tratamiento a 1400°C.

Palabras clave: $\text{CeO}_2\text{-Gd}_2\text{O}_3$, manganitas, compatibilidad química, compatibilidad termomecánica.

1. INTRODUCTION

In the last decades, lanthanum manganites have been widely investigated (1-3) and specifically the ones modified with alkaline earth cations have been the best-known ceramic electrodes for SOFC cathode applications due to their good electrical conductivity and relatively low cost. Nevertheless, they present problems due to lanthanum reaction at high temperatures with YSZ electrolytes (4-6) forming secondary phases such as $\text{La}_2\text{Zr}_2\text{O}_7$. Furthermore, alkaline earth cations employed can also react with zirconia or with ceria based electrolytes, forming perovskite-type zirconates (SrZrO_3) and Ba, Sr cerates, respectively. These secondary phases can cause poor-conductivity or even to form insulating interfaces. In order to overcome these problems, it is necessary to

employ new materials for SOFC cathodes of intermediate temperature. The materials proposed would be manganites where lanthanum is replaced by rare earth with lower ionic-radius cation such as neodymium and furthermore, in which Mn has been partially replaced by a divalent cation on B sites (transition metals such as Me = Ni, Co), $\text{NdMe}_{0.5}\text{Mn}_{0.5}\text{O}_3$. The substitutions in the perovskite structure of lanthanum by neodymium on A sites and of transition metals on B sites are proposed as alternative to obtain chemically more stable systems (7). That is, the possible pyrochlore phase formed from heavy rare earth cations possess a lower stability at sintering and operating temperatures and the reaction with electrolytes based on ceria should not take place.

For successful long term operation of SOFC a good compatibility among the ceramic materials is crucial. That is, it should be avoided cation diffusion and ensured no reaction within the cathode/electrolyte interface.

Since the last tendencies are addressed to the use of ceria based electrolytes, working at lower temperatures between 600-800°C and having higher ionic conductivity than YSZ, in the present paper is established the phase relations between two of these $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ ceramics and $\text{NdMe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (Me=Ni, Co) solid solutions as cathodes. In one case the gadolinia doped ceria solid electrolyte has been doped with Bi_2O_3 to improve densification, according to the results described elsewhere (8). The thermal expansion behaviour of these ceramics was characterized and furthermore, scanning electron microscopy observation with EDAX analysis was performed in cathode-electrolyte interfacial regions in order to characterize the obtained microstructures and to determine possible cation diffusions from the cathode into the electrolyte.

2. EXPERIMENTAL

2.1. Powder synthesis and compatibility studies

Ceramic powders of the composition $\text{NdMn}_{0.5}\text{Me}_{0.5}\text{O}_3$ (Me=Ni, Co) were prepared using the ethylene glycol metal nitrate polymerized complex process (9), by mixing precursors of $\text{Nd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Ventron, 99.9%), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merk, 99.0%) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 99.0%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 98.0%), or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merk, 99.5%) in appropriate stoichiometric ratios. The obtained powders were calcined at 650°C for 6h in air and wet-milled with ethanol for 2h in an attrition ball milling using zirconia balls. Those powders will be denoted as NNiM and NCoM.

Ceria based electrolyte powders, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$, were processed by two alternative routes: by coprecipitation technique using ammonium hydroxide as precipitant agent (powders lately calcinated at 600°C for 2h) and adding to a submicronic commercial $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ powder (Rhodia GmbH, FRG) 1.0 wt% Bi_2O_3 as a sintering aid. Those powders will be denoted as CGO (obtained via chemical) and CGO-Bi (obtained from a commercial powder), respectively.

X-ray powder diffraction (Siemens D-500, $\text{CuK}\alpha$ radiation) analysis was carried out for the reaction studies. For this purpose equal amounts (50 wt%) of the cathode and electrolyte powders were ground, pressed into pellets and then heat treated in air between 1350 and 1450°C for 4h and aging at 1000°C for 100 h in air. The sintered pellets were crushed and the resultant powders were analysed by X-ray diffraction.

Finally, the shrinkage characteristics were characterized using a dilatometer Netzsch (model 407/E, Selb-Bayern Germany) and the coefficients of linear thermal expansion were measured on the single ceramics. Measurements were performed at a heating rate of 5°C/min.

2.2. Cell fabrication and characterization

Calcined and milled NNiM, NCoM and CGO powders were isostatically pressed at 200MPa to prepare pairs of NNiM/CGO and NCoM/CGO, which were lately sintered at 1400°C for 2h. Pairs with $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95} + 1.0\text{wt}\%\text{Bi}_2\text{O}_3$ (CGO-Bi) electrolytes were prepared and sintered at 1350°C for 2h (NNiM/CGO-Bi and NCoM/CGO-Bi). The selected temperatures were based on the densification results and

electrical properties previously obtained for both types of electrolyte and are described in details elsewhere (10-11). The polished and fractured cross-sections were observed with scanning electron microscopy (SEM) in order to characterize the microstructure. Element analysis was performed by EDAX in order to investigate element inter-diffusion across the interface from the cathode to the electrolyte.

3. RESULTS AND DISCUSSION

3.1. Powder Characteristics

Table 1 shows the mean characteristics of the ceramic powders selected to produce cathode-electrolyte pairs.

TABLE I. MEAN CHARACTERISTICS OF THE CERAMIC POWDERS SELECTED TO PRODUCE CATHODE-ELECTROLYTE PAIRS.

Compositions	Calcining conditions	Mean particle size (TEM) (nm)	Mean agglomerate size (SEM) (μm)
$\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$	600°C/120h	20 $\pm$ 10	0.5-1.7
$\text{NdCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$	650°C/6h	50 $\pm$ 10	0.6-1.6
$\text{NdNi}_{0.5}\text{Mn}_{0.5}\text{O}_3$	650°C/6h	45 $\pm$ 10	0.5-1.5

TEM and SEM micrographs of the NNiM and CGO calcined powders are shown as examples in figure 1 and 2, respectively. All powders showed spherical geometry and the particle size distribution was narrow. The average particle sizes of the manganite powders are very similar in both cases, $\text{NdMe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (Me=Ni, Co) with values around 50 nm as it can be determined by TEM (Figure 1a-b). In contrast, the particles of doped ceria powders obtained via chemical (CGO) are much smaller than those of commercial (CGO-Bi). The average particle size of this one is ~ 150 nm (Figure 2c), while the synthesized powder has fine particles with average size ~ 20 nm (Figure 2d). It should be mentioned that the ceramic powders obtained have such a small particle size, that it typically forms agglomerates when preparing powders for SEM observation (Figure 2a-b).

The XRD patterns (not shown here) of the NMeM powders after calcining at 650°C for 6h, exhibit all peaks according to a well-crystallized perovskite phase with an orthorhombic Pbnm space group. In the case of the CGO powders prepared chemically, the XRD pattern shows all diffraction peaks associated with a pure fluorite structure as that of the commercial CGO powder, although the peaks are somewhat broadened due to its extremely fine microcrystalline structure.

The thermal expansion coefficients (TEC), α , obtained from the slopes of the thermal expansion curves, are summarized in Table 2. Furthermore and for comparison are included TEC values previously reported in the literature of some of the most commonly ceramic materials used as SOFC cathodes.

The thermal expansion rates of cathodes are significantly different between them. So, the TEC values increase as sequence NCoM<CGO<NNiM.

Although it is confirmed that exist a certain difference between the TEC of electrolytes ($\alpha = \sim 12.6 \times 10^{-6} \text{ K}^{-1}$) and cathodes selected ($\alpha = 12-13 \times 10^{-6} \text{ K}^{-1}$) these one are smaller

Fig. 1- TEM images of the synthesized and calcined powders: (a) $\text{NdNi}_{0.5}\text{Mn}_{0.5}\text{O}_3$, (b) $\text{NdCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$, (c) commercial $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ powder and (d) synthesized $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ powder.

than those reported in other types of ceramic materials used as cathodes such as some manganites (12) ($\alpha = \sim 7.5\text{--}8.5 \times 10^{-6} \text{ K}^{-1}$), chromites (13) ($\alpha = \sim 11 \times 10^{-6} \text{ K}^{-1}$) or ferrites (14) ($\alpha = \sim 14 \times 10^{-6} \text{ K}^{-1}$), that although their electrical properties are excellent, they can not be used with electrolytes based on ceria since as a great thermal mismatch would be able to produce cracks or inclusive the breakness of the cell. Furthermore, it is noted than a small amount of bismuth oxide on the ceria gadolinia system does not affect the thermal expansion behaviour of the ceramic material.

3.2. Chemical compatibility

In general, the mean problem in the use of perovskite materials in SOFC applications is their reactivity with the most of electrolyte materials and therefore, the formation of

undesirable new phases along cathode-electrolyte interface, which can affect the conductivity (15). For this reason, and in order to study the possible reactions between the NMeM and CGO phases, several powder mixtures were prepared and treated at elevated temperatures for 4h and lately annealed in air at 1000°C during long sintering times (4-100h).

Figure 3(a-b) displays the XRD patterns of the NCoM + CGO and NNiM + CGO pairs respectively, before and after heat-treatment. In both cases, it is observed that all phases maintain their crystalline structures and remain without degradation at all the temperatures and times studies. According to these results obtained, the perovskite systems seem to be compatible, even in the most severe conditions (i.e. 1450°C), with the ceria electrolyte at least at the level of observation corresponding to the sensibility of the XRD analyses.

Fig. 2- SEM images of the synthesized and calcined powders: (a) $\text{NdNi}_{0.5}\text{Mn}_{0.5}\text{O}_3$ and (b) $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ prepared by the ethylene-glycol process and precipitation technique, respectively.

3.3. Interface microstructural characterization

In order to ensure that the two layers bonded perfectly and formed a well-defined interface without and that there is no any presence of cation diffusion through interfacial region, cosintered pairs were characterized by scanning electron microscopy (SEM).

Figure 4 shows SEM images obtained at fractured and polished cross-sectional surfaces corresponding to $\text{NdNi}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (NNiM) cathodes cosintered with $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) or $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95} + 1.0 \text{ wt}\% \text{ Bi}_2\text{O}_3$ (CGO-Bi) electrolytes.

Both thermal treatment applied (1350 and 1400°C during 2h) resulted in a good connectivity between the cathode and the electrolyte layers, with a well-defined interface and without the presence of any new secondary phases, according with XRD results obtained. Furthermore, the good adhesion between the layers of the pairs and the lack of structural defects (absence of cracks or delaminations) confirms a good adjustment of the coefficients of thermal expansion through the cosintering process. Both thermal treatment temperatures

Fig. 3- XRD patterns of mixed powder fired between 1350 and 1450°C for 4h and after that annealed in air at 1000°C for 100h, (a) $[\text{NdCo}_{0.5}\text{Mn}_{0.5}\text{O}_3] + [\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95} + 1\% \text{ wt. Bi}_2\text{O}_3]$ and (b) $[\text{NdNi}_{0.5}\text{Mn}_{0.5}\text{O}_3] + [\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95} + 1\% \text{ wt. Bi}_2\text{O}_3]$.

TABLE 2. COEFFICIENTS OF THERMAL EXPANSION OF ELECTROLYTES (GDC-BI AND GDC) AND DOPED MANGANITES $\text{NdMe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (ME=NI, CO).

Experimental results		Literature	
Compositions	$\alpha \times 10^6 \text{ (K}^{-1}\text{)}$	Compositions	$\alpha \times 10^6 \text{ (K}^{-1}\text{)}$
CGO-1% Bi_2O_3	12.6	[7] $\text{Nd}_{0.95}\text{MnO}_3$	7.6
CGO	12.7	[7] $\text{La}_{0.95}\text{MnO}_3$	8.7
$\text{NdCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$	12.0	[8] $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_{3-\delta}$	11.1
$\text{NdNi}_{0.5}\text{Mn}_{0.5}\text{O}_3$	13.1	[9] $\text{Sm}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	14.5

resulted in electrolytes with very homogenous microstructures with submicronic average grain size ($\sim 0.8 \mu\text{m}$) and adequate sintered density ($>94 \%$ of relative density), which is enough to ensure a good cell operation. Nevertheless, it should be noted that in the case of electrolyte doped with a small amount of bismuth oxide his density is higher (97% vs. 95% relative density).

According to cathode microstructure observation, the lower sintering temperature (1350°C) resulted in the uniform structure with a small grain size ($0.7\text{--}1 \mu\text{m}$) and a highly interconnected porosity of $\sim 0.5 \mu\text{m}$, while the higher thermal treatment temperature (1400°C) of the cathodic eliminated a good part of its porosity.

Fig. 4- (a,d) Fracture surface and (b,c) polished surface of cross-sectional views of typical electrolytes cosintered with cathodes $\text{NdNi}_{0.5}\text{Mn}_{0.5}\text{O}_3$, to form pairs (a,b) NNiM/CGO (1400°C-2h) and (c,d) NNiM/CGO-Bi (1350°C-2h).

Fig. 5- (a) Fracture surface and (b) polished surface of cross-sectional views of an electrolyte CGO-Bi cosintered at 1350°C-2h with a cathode $\text{NdCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$.

In the case of cobalt doped manganite for the formation of the pairs, cathode microstructures are similar for both sintering temperatures (1350 and 1400°C) applied. Due to this, only the cross-sectional view corresponding to the pair prepared with the electrolyte doped with bismuth oxide (NCoM/CGO-Bi) and cosintered a lower temperature (1350°C for 2h) is shown in Figure 5. It is observed that layers remain in a good connectivity and the interface is free of cracks, as it can be predicted from the results of coefficients of thermal expansion obtained. Nevertheless, these manganite systems are very heterogeneous and present the exaggerate grain growth ($\sim 5\text{--}20\text{ }\mu\text{m}$ vs. $\sim 0.8\text{ }\mu\text{m}$ for CGO ceramics) at the temperature ranges between 1350–1400°C. These conditions could affect negatively on mechanical properties within the final product, resulting in a mechanically weak cell. Thus they are not the most adequate for use as cathodes in SOFC applications, where the thermal treatments are equal or exceed 1350°C.

Therefore, considering the results discussed above, cobalt doped manganites were excluded from future work and only nickel doped manganites were selected to be used in cosintering at 1350–1400°C with a electrolyte based on ceria.

In order to confirm the lack of any kind of cations migration across the interfacial region, EDAX analyses on located marks were carried out (Figure 6).

EDAX spectrums show that in the cathode region located near interface appear a number of peaks at the positions expected for a system that contains Nd, Ni and Mn elements. That is, there is no presence of cerium or gadolinium diffusion from the electrolyte into the cathode. In the same way, neodymium, nickel or manganese diffusions were not detected at the electrolyte surface even close to the electrode side.

4. CONCLUSIONS

Neodymium based perovskites, $\text{NdMn}_{0.5}\text{Me}_{0.5}\text{O}_{3\gamma}$, are chemically compatible with the fluorite type ceramic $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95\gamma}$, i.e. no reaction products have been observed after heat treatments even at 1450°C. Therefore, it is possible to cosinter single cells of NNiM/CGO (or NNiM/CGO-Bi) and NCoM/CGO (or NCoM/CGO-Bi), without appearance of new phases in the boundary between electrode and electrolyte.

The pairs constituted from nickel doped manganite as cathode material present (when are fixed on both electrolytes) well-defined and free of cracks interfaces as expected from the study of the coefficients of thermal expansion. Furthermore, these nickel doped manganites show a good microstructure formation behaviours (no exaggerated grain growth and pore closure is present) at the thermal treatment temperatures between 1350–1400°C. Thus these materials should perform excellently as cathodes within the SOFC, where the thermal treatment temperatures up to 1400°C are required.

ACKNOWLEDGMENTS

Financial support from the CICYT MAT 2003-01163. Project and a grant from the Autonomous Community of Madrid are gratefully acknowledged.

Fig. 6- EDAX analysis on interface (a) NNiM/CGO-Bi and (b) NNiM/CGO cosintered at 1350 and 1400°C, respectively.

REFERENCES

1. Yamamoto O., Takeda Y., Kanno R. and Noda M., Perovskite-type oxides as oxygen electrodes for high-temperature oxide fuel-cells, *Solid State Ionics*, 22, 2-3, 241-246 (1987).
2. Adler S.B., Factors governing oxygen reduction in solid oxide fuel cell cathodes, *Chemical Reviews*, 104, 10, 4791-4843 (2004).
3. Mobius H.H., On the history of solid electrolyte fuel cells, *Journal of Solid State Electrochemistry*, 1, 1, 2-16 (1997).
4. Lau, S.K. and Singhal, S.C., Potential electrode/electrolyte interactions in solid oxide fuel cells. *Corrosion*, 85, 345 (1985), Boston MS.
5. Taimatsu H., Wada K., Kaneko H. And Yamamura H., Mechanism of reaction between lanthanum manganite and yttria-stabilized zirconia, *Journal of the American Ceramic Society*, 75, 2, 401-405 (1992).
6. Yokokawa H., Saka N., Kawada T. and Dokiya M., Thermodynamic analysis on interface between perovskite electrode and YSZ electrolyte, *Solid State Ionics*, , 40-41, 398-401 (1990).
7. Kostogloudis G.C. and Ftikos C., Effect of Sr-doping on the structural and electrical properties of gadolinium manganite oxide, *Journal of materials science*, 34, 9, 2169-2173 (1999).
8. Gil V., Tartaj J., Moure C. and Durán P., Rapid densification by using Bi_2O_3 as an aid for sintering of gadolinia-doped ceria ceramics, *Ceramics International*, 33, 3, 471-475 (2007).
9. Duran P., Tartaj J., Capel F. and, Processing and characterisation of a fine nickel oxide/zirconia/composite prepared by polymeric complex solution synthesis, *Journal of the European Ceramic Society*, 23, 12, 2125-2133 (2003).
10. Gil V., Moure C., Durán P. and Tartaj J., Low-temperature densification and grain growth of Bi_2O_3 -doped-ceria gadolinia ceramics, *Solid State Ionics*, 178, 5-6, 359-365 (2007).
11. V. Gil, Tesis Doctoral: Preparación y caracterización de materiales cerámicos para su uso como componentes: electrolito, ánodo y cátodo, en pilas de combustible de óxido sólido de temperatura intermedia. Estudio de sus compatibilidades, (2006).
12. Wandekar R.V., Wani B.N. and Bharadwaj S.r., High temperature thermal expansion and electrical conductivity of $\text{Ln}_{0.95}\text{MnO}_{3+\delta}$ ($\text{Ln}=\text{La}$, Nd or Gd), *Journal of alloys and compounds*, 433, 1-2, 53-57 (2007).
13. Zhou X. and Ma J., Preparation and properties of ceramic interconnecting materials, $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_{3-\delta}$ doped with GDC for IT-SOFCs, *Journal of Power Sources*, 162, 1, 279-285 (2006).
14. Xu Q., Huang D.P., Chen W. And Wang B., Structure, electrical conducting and thermal expansion properties of $\text{Ln}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ ($\text{Ln}=\text{La}$, Pr , Nd , Sm) perovskite-type complex oxides, *Journal of Alloys and Compounds*, 429, 1-2, 34-39 (2007).
15. Richland W.A., Chemical interactions between interconnect and electrode materials during sintering in solid oxide fuel cells, alternative electrodes and interconnections for solid oxide fuel cells, *Laboratories Pacific Northwest Ed.*, 632-640 (1993).

Recibido: 31.07.07

Aceptado: 20.12.07