Electronic supplementary information (ESI)

X-ray Diffraction patterns of BCZ20Y15, YDC15 and GDC15

Figure S1 plots XRD patterns of BCZ20Y15 from Mariom Technologies and GDC15 and YDC15 synthesized by solid state reaction. The diffraction data of BCZ20Y15 reveal the presence of impurities of BaCO$_3$ (Pmcn space group, no. 62) and CeO$_2$ (Fm-3m space group, no. 225) phases as indicated in Figure S1.

![X-ray diffraction patterns](image)

**Figure S1.** X-ray diffraction (XRD) patterns of “as received” BCZ20Y15 powders and of YDC15 and GDC15 powders after calcination at 1200°C (* and ○ refers to BaCO$_3$ and CeO$_2$ phases respectively).
Sintering of the composite membranes

Table S1 reports mean relative densities of BCZ20Y15-MDC15 composite membranes after sintering at 1450 °C with 1 wt% of ZnO (sintered disks of Ø ≈ 15 mm), and shows mean densities higher than 96% for all composition specimens. The microstructure of the dense membranes was studied by SEM-EDS (Figure S2); the micrographs confirm the homogeneous distribution with well-formed grains and free-pore structures of the composites. As depicted in the back-scattered electron micrograph of Figure S3, some isolated and sporadic residual grains of ZnO were detected in few samples (dark spots on the top right part of the image).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean Relative Density (%)</th>
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<tbody>
<tr>
<td>BCZ20Y15-YDC15 50:50</td>
<td>97</td>
</tr>
<tr>
<td>BCZ20Y15-YDC15 60:40</td>
<td>96</td>
</tr>
<tr>
<td>BCZ20Y15-GDC15 50:50</td>
<td>97</td>
</tr>
<tr>
<td>BCZ20Y15-GDC15 60:40</td>
<td>96</td>
</tr>
</tbody>
</table>

Table S1. Mean relative densities of BCZ20Y15-MDC15 composite membranes after sintering at 1450 °C with 1 wt% of ZnO (sintered disks of Ø ≈ 15 mm).

Figure S2. SEM micrographs of the fracture cross-sections of BCZ20Y15-YDC15 and BCZ20Y15-GDC15 50:50 vol (a and c) and 60:40 vol (b and d) dense membranes after sintering at 1450 °C with the addition of ZnO as aid sintering.

Figure S3. Back-scattered electron micrograph of a BCZ20Y15-GDC15 50:50 membrane. The black areas on the top-right part of the Figure are composed mainly by residual grains of ZnO, as revealed by EDS analyses.
Electrochemical characterization: electromotive force (EMF) measurements (or open circuit voltage, OCV)

EMF measurements of the 50:50 membranes compared with calculated theoretical values and sintered BCZ20Y15, YDC15 and GDC15 (prepared in analogous conditions, i.e. sintering at 1450 °C with 1 wt% of ZnO as sintering aid) are plotted in Figure S4.

![Figure S4. Comparison of measured EMF values of BCZ20Y15, YDC15, GDC15 and 50:50 composites dense specimens with the calculated theoretical values.](image)

The lowering of the open circuit voltage in BCZ20Y15-YDC15 or BCZ20Y15-GDC15 membranes in comparison with both the theoretical and the BCZ20Y15 values indicates the enhanced electronic contribution to conductivity. Indeed, the electronic conductivity generates a current leakage that results in lower values of electromotive force. With increasing temperature, the larger difference between the theoretical and BCZ20Y15 values can be attributed to the higher mobility of electron holes $h^-$ and to the loss of water.\(^{11,39}\) In the same way, the measured EMF values of YDC15 and GDC15 were lower due to the greater electronic conduction contribution. At 500 and 600 °C, the measured open circuit voltage of YDC15 is slightly higher than the GDC15 value while at 700, 800 and 900 °C the collected data are almost equivalent. This behaviour was followed also by the corresponding composites at 500 °C (i.e. $\text{EMF}_{\text{BCZ20Y15-YDC15 50:50}} > \text{EMF}_{\text{GDC15 50:50}}$) but in lesser extent. This fact could be ascribed to the lower intrinsic reduction state of the YDC15 powders compared to GDC15 after sintering in air in YDC15 containing samples. In H\(_2\) separation conditions, both sides of the membranes are exposed to more reducing atmospheres, so it is expected a further enhancement of the electronic conductivity.
Hydrogen permeation

Figure S5 plots the H\(_2\) flux (mL·min\(^{-1}\)·cm\(^{-2}\)) as a function of temperature for BCZ20Y15-GDC15 50:50 composite (700 μm thickness) without Pt catalytic layer measured in three configurations (C2, C3 and C4) feeding 50% H\(_2\) in He and the comparison with the membrane coated with a Pt layer. H\(_2\) fluxes obtained by using the membrane with Pt are significantly higher than those obtained with the membrane without catalytic layer which is ascribed to the modest surface catalytic activity of the BCZ20Y15-GDC15 materials. The difference between fluxes is more pronounced at lower temperatures where surface processes are slower, since the activation energy of surface exchange processes is higher than that exhibited by bulk proton diffusion. \(^{51}\)

![Figure S5](image)

**Figure S5.** H\(_2\) flux (mL·min\(^{-1}\)·cm\(^{-2}\)) as a function of temperature for BCZ20Y15-GDC15 50:50 composite (700 μm thickness) without Pt catalytic layer measured in three configurations (C2, C3 and C4) feeding 50% H\(_2\) in He (a) and H\(_2\) flux (mL·min\(^{-1}\)·cm\(^{-2}\)) as a function of reciprocal temperature for the BCZ20Y15-GDC15 50:50 samples with and without Pt catalytic layer measured under C3 and C4 conditions feeding 50% H\(_2\) in He (b).

Figure S6 plots X-ray diffraction (XRD) patterns of BCZ20Y15-GDC15 50:50 membranes before and after Hydrogen permeation tests up to 1040 °C conducted in C3 and C4 feeding 50% H\(_2\). XRD patterns show only BCZ20Y15 and GDC15 peaks without any secondary phase. After permeation tests, only a line broadening effect is observed. More cross section SEM micrographs of the BCZ20Y15-GDC15 50:50 membrane after the tests conducted up to 1040 °C are reported in Figure S7. It is possible to observe the bulk of the sample with a similar microstructure of the “as sintered” sample and the surface exposed to the feed side chamber. In this outer part of the membrane, the catalytic Pt porous layer and some areas with a more porous structure are present. These regions correspond to Ba deficient-BCZ20Y15 phase probably due to BaO evaporation at high temperatures but this phenomenon seems limited to some surface regions (100-200 nm thick).
**Figure S6.** X-ray diffraction (XRD) patterns of BCZ20Y15-GDC15 50:50 membrane before and after H$_2$ permeation tests up to 1040 °C conducted in C3 and C4 feeding 50% H$_2$.

**Figure S7.** Secondary electron micrographs of the fracture cross sections of BCZ20Y15-GDC15 50:50 dense membranes after permeation tests in C3 and C4 conditions up to 1040 °C and feeding 50% H$_2$ in He.
Thermogravimetric analysis of composite membranes

Figure S8 plots X-ray diffraction (XRD) patterns of BCZ20Y15-YDC15 and BCZ20Y15-GDC15 50:50 and 60:40 sintered powders (sintering at 1450°C with ZnO as aid sintering) after TGA analyses under CO₂-containing atmosphere. TG analyses were conducted under N₂ (100 mL/min)/CO₂ (20 mL/min) continuous flow up to 1300 °C at 10 °C min⁻¹.

**Figure S8.** X-ray diffraction (XRD) patterns of BCZ20Y15-YDC15 and BCZ20Y15-GDC15 50:50 and 60:40 composites sintered powders (sintering at 1450°C with the addition of ZnO as sintering aid) after TGA analyses under N₂ (100 mL/min)/CO₂ (20 mL/min) continuous flow. “*” and “∞” symbols refers to BaCO₃ phases R-3m and Pmcn space group respectively.

XRD patterns of the composite membrane powders after TGA analyses under CO₂-containing atmosphere up to 1300 °C show no phase changes with some few weak peaks ascribable to two BaCO₃ phases (R-3m space group no.166 and Pmcn no. 62 respectively).