Innovative membranes for oxygen separation: experimental study of their performance and long-term stability at high temperature

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Abstract

Oxygen Transport Membranes (OTMs) are widely studied because of their possible use in different technological applications. Several studies in the literature have investigated the feasibility of integrating these membranes in energy-intensive processes, finding advantages both in terms of reduction of energy consumption and costs [1]. Moreover, in recent years, particular attention has been paid to the most innovative applications, such as catalytic membrane reactors [2], that are devices in which reaction and separation take place simultaneously, allowing a process intensification. This solution can be adopted for the production of energy carriers (e.g. H_2) or synthetic fuels, with a configuration similar to that reported in **Fig. 1**:

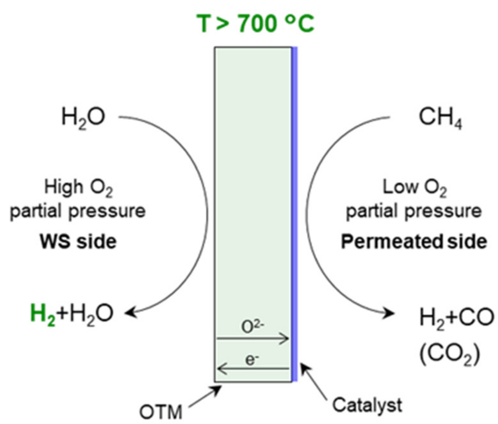

Fig. 1 – possible configuration of a catalytic membrane reactor for the hydrogen production.

The most interesting applications require severe operating conditions, such as high temperature (normally above 700 °C), high pressure and possible presence of aggressive gases (e.g. CO_2, H_2S, H_2O, CO and others) in the process gas streams. Therefore, the ceramic materials used for the membrane production should ensure sufficiently high oxygen flux and good stability under such conditions. Most investigated membranes, such as single-phase perovskites, e.g. LSCF or BSCF, show excellent performance in terms of permeation, but suffer from phase degradation during the operation and are not stable in presence of CO_2 [3].
For these reasons, the identification of more stable materials is crucial for a large-scale application of the membrane technology in the industrial sector.

In this work, different materials are studied as alternative to LSCF membranes. We focused our attention especially on dual-phase composites LSCF-CGO and single-phase STF-based perovskites where Sr is partially replaced by Ca to improve the sintering behaviour of the membrane and the resistance against CO_2.
We prepared both dense and asymmetric membranes, by uniaxial pressing or sequential tape casting technique, respectively. The manufactured samples have been tested at high temperature (700 – 950 °C) and at atmospheric pressure in order to verify their permeation performance in clean conditions; results have been compared with data obtained by testing traditional LSCF membranes in the same operating conditions and with data available in literature. Furthermore, the long-term stability of these innovative membranes has been investigated both in terms of oxygen flux and defects formation over time.

Results collected in clean conditions at 900 °C using STF-based and dual-phase membranes are really promising: the membranes didn't show any performance reduction over more than 300 and 500 hours of operation, both in terms of oxygen flux and defects formation, confirming a very high thermal stability.
In addition, the influence of different CO_2 concentrations on the permeation process has been studied over short and long-term tests, in order to investigate the stability of the innovative materials under reducing condition.
The characterization of tested membrane samples has been performed by scanning electron microscopy (SEM) and X-ray diffraction (XRD), in order to identify possible microstructural or compositional evolution of the ceramic materials. Preliminary results did not reveal the presence of additional phases, both on STF-based and dual-phase membranes.

References

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