

## Summary

Mixed ionic (oxygen ions or protons) and electronic conducting materials (MIEC) separate oxygen or hydrogen from flue gas or reforming streams at high temperature in a process 100% selective to the ion. These solid oxide materials may be used in the production of electricity from fossil fuels (coal or natural gas), taking part of the CO<sub>2</sub> separation and storage system. Dense oxygen transport membranes (OTM) can be used in oxyfuel combustion plants or in catalytic membrane reactors (CMR), while hydrogen transport membranes (HTM) would be applied in precombustion plants. Furthermore, these materials may also be used in components for energy systems, as advanced electrodes or electrolytes for solid oxide fuel cells (SOFC) and proton conducting solid oxide fuel cells (PC-SOFC) working at high and moderate temperature.

The harsh working conditions established by the targeted processes include high temperatures and low O<sub>2</sub> partial pressures ( $pO_2$ ), probably combined with CO<sub>2</sub> and SO<sub>2</sub> containing gases. The instability disadvantages presented by the most widely studied materials for these purposes make them impractical for application to gas separation. Thus, the need to discover new stable inorganic materials providing high electronic and ionic conductivity is still present.

This thesis presents a systematic search for new mixed ionic-electronic conductors. It includes different crystalline structures and/or composition of the crystal lattice, varying the nature of the elements and the stoichiometry of the crystal. The research has yielded new materials capable to transport oxygen ions or protons and electronic carriers that are stable in the working condition to which they are submitted.

The characterization of a large series of lanthanide-doped ceria ( $\text{CeO}_2$ ) provides an overall understanding of the structural and transport properties of these materials. Besides, the addition of cobalt oxide on this system is similarly studied. The analysis is completed by the optimization of the transport properties dependence on the microstructure. This allows a preliminary classification of the materials based on the main transport behavior and shows the possibility of tailoring both the structure and operating conditions to achieve desired properties for a number of applications, i.e. solid oxide fuel cells (SOFC) electrodes or oxygen separation membranes

Several materials emerged from this work have achieved their purpose.  $\text{Ce}_{1-x}\text{Tb}_x\text{O}_{2-\delta}$  and  $\text{Ce}_{1-x}\text{Tb}_x\text{O}_{2-\delta} + 2 \text{ mol\% Co}$  are proposed as a family of materials that may provide competent oxygen permeation fluxes and stability against  $\text{CO}_2$  containing atmospheres. Besides, the inclusion of this material as a component of a dual-phase membrane increases the oxygen flux possibilities. The combination with a stable, Co and alkali-earth free spinel has delivered a promising membrane material for the integration in oxyfuel power plants.

On the other hand, metal dopants on the  $\text{Ce}_{0.9-x}\text{M}_x\text{Gd}_{0.1}\text{O}_{2-\delta}$  structure have been added to lanthanide-doped ceria. They have been studied as SOFC cathode in combination with  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ -perovskite. The results show that the ionic conductivity inherited by the ceria allows decreasing the polarization resistance regarding to the single phase cathode.

The study of a second group of materials involves a wide screening of doped  $\text{CaTiO}_3$  perovskites. The difficulty of obtaining stable perovskites with high mixed ionic-electronic conductivity is evidenced. Iron and iron-magnesium doped  $\text{CaTiO}_3$  are the best candidates as they present mainly ionic conductivity at high temperatures, while *p*-type electronic conductivity is predominant in the

low temperature range.  $\text{CaTi}_{0.73}\text{Fe}_{0.18}\text{Mg}_{0.09}\text{O}_{3-\delta}$  is shown as a promising material offering good oxygen permeation fluxes and stability against  $\text{CO}_2$ , although it reacts with  $\text{SO}_2$ .

Finally,  $\text{La}_{0.87}\text{Sr}_{0.13}\text{CrO}_3$  (LSC) perovskites have been doped in order to increase the mixed protonic-electronic conductivity. The study has led to the development of a new generation of anodes for LWO based PC-SOFC. Ce in the A-site (LSCCe) and Ni in the B-site (LSCN) are stable perovskites in the reducing anode working conditions and in contact to the LWO electrolyte. Both of them decrease the polarization resistance regarding to pure LSC. LSCCe is limited by low frequency processes (LF), which are alleviated in the case of LSCN due to the formation of metallic nanoparticles on the surface. The further infiltration of Ni nanoparticles allows decreasing the LF resistance, which suggests that the surface reaction of  $\text{H}_2$  oxidation is catalyzed. The most concentrated infiltration (5Ni) completely eliminates the LF resistance in both anodes and only high frequency (HF) processes remain. The best anode performance was obtained for LSCNi20+5Ni. Polarization resistance was as low as  $0.26 \Omega \cdot \text{cm}^2$  at  $750 \text{ }^\circ\text{C}$  in wet  $\text{H}_2$ .