Oxygen Activity across a YSZ Electrolyte Visualized by Optical Spectroscopic Probes

Solid oxide fuel cells (SOFC) are reversible devices that generate electric energy by oxidation of a fuel, commonly hydrogen. In electrolyser mode (SOEC), a voltage is applied and hydrogen is generated from water. These processes are highly efficient, although one of the main sources of degradation in these devices arises from extreme oxygen activity inside the electrolyte at the interfaces with the electrodes [1, 2], developed because of inappropriate operating conditions or poor electrode performance. In particular, high oxygen partial pressure in the oxygen electrode/electrolyte interface can lead to electrode delamination when working in SOEC mode at high voltages. The purpose of this work is to investigate the oxygen activity profile established across a yttria-stabilized zircona (YSZ) electrolyte upon different polarization conditions.

To achieve this goal, several redox ions were studied as spectroscopic probes inside a YSZ matrix and among them terbium was found to be a suitable dopant as optical spectroscopic probe for intermediate and high ranges of oxygen activity [3]. By means of optical absorption and diffuse reflectance, 3+/4+ terbium oxidation states could be identified in samples annealed in different atmospheres. Tb3+ luminescence signals can be used to follow the 3+/4+ dopant redox couple, and using the strong 5D4 → 7F5 Tb3+ luminescence emission [4], a quantitative relation between its intensity and oxygen partial pressure in equilibrium with the doped electrolyte could be established (Fig. 1). Therefore, this signal can be used to quantify the pO2 in equilibrium at different positions inside the electrolyte.

Several experiments were designed in order to obtain different electrochemical parameters from the YSZ-Tb system. First of all, ionic conductivity of the terbium doped YSZ electrolyte was determined with symmetrical cells with platinum electrodes and testing them by impedance spectroscopy under oxygen and hydrogen atmospheres in a wide range of temperatures.

Electronic conductivity of YSZ-Tb could be determined using Hebb-Wagner cells with a LSM/YSZ electrode on the oxygen side and an ion-blocking Pt electrode. Similar cells were also polarized under different conditions and cooled down to freeze the oxygen activity gradient. The quenched O2 activity profile was quantified using Tb3+ luminescence signal intensity, and analysed taking into account the actual conductivity of the minority carriers, as determined in the previous experiments.

Cells with a LSM/YSZ cermet air electrode and a Ni/YSZ cermet hydrogen electrode were tested in SOEC mode. When in stationary state, cells were quenched, freezing the high-temperature under-voltage terbium oxidation state, as shown in Fig. 2. By analysing the terbium luminescence signal, oxygen activity and oxygen partial pressure across the electrolyte thickness could be determined under different polarization conditions. The results and capabilities of the method will be discussed.

[1] A. Virkar, Int. J. Hydrogen Enery 35 (2010) 9527.
[2] M.A. Laguna-Bercero et al., Int. J. Hydrogen Energy 36 (2011) 13051.
[3] R.I. Merino et al. (2018) https://digital.csic.es/handle/10261/182893.
[4] M.R.N. Soares et al., Materials Letters 65 (2011) 1979-1981.

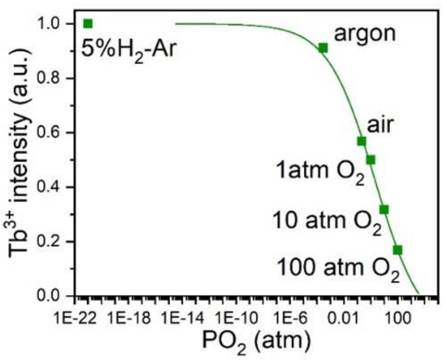

Fig. 1 Tb^{3+} luminescence intensity signal in the doped electrolyte stabilized at different oxygen partial pressures.

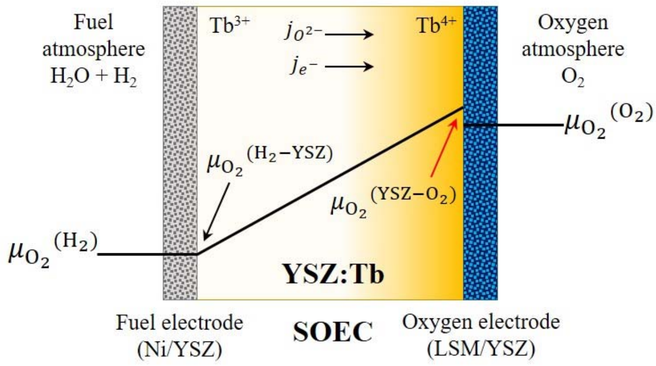

Fig. 2 Sketch of the oxygen chemical potential gradient and terbium oxidation state in a YSZ-Tb cell working in SOEC mode.