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Study of the role played by Ce in metal/oxide solid oxide fuel cell anodes during CH_4 and H_2 electro-oxidation

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The development of solid oxide fuel cells (SOFCs) as a cleaner technology is a field that has been growing in the last years. These devices are capable of transforming chemical energy into electricity with high efficiency, i.e. a SOFC coupled to a gas turbine can produce energy with efficiency higher than 60 %. In particular, the development of new composites metal/oxide anode materials with electrocatalytic activity for direct CH4 oxidation could also reduce the emission of greenhouse gases. It has been reported by Gorte et al. that the addition of ceria improves the efficiency of Cu-YSZ (yttria-stabilized zirconia ZrO_2) SOFC anodes in atmosphere of H_2, CO and syngas [1-2]. Recently, we synthesized and performed some studies on different anodes composed by Cu and CeO_2-YSZ oxides. The interest is to develop Ce doped YSZ (CeYSZ, $Ce_{0,084}Y_{0,136}Zr_{0,78}O_{2-\alpha}$) as mixed ion/electron conductor anode support material. TPR (Temperature Programmed Reduction) measurements shown that cerium undergoes a reduction process in presence of a reducing atmosphere (H_2); thus giving electron conduction properties to the oxide matrix (CeYSZ). EIS (Electrochemical Impedance Spectroscopy) measurements of Cu-CeO_2-YSZ anodes in dry methane showed that the electrode resistance in stable at 700 °C for a period over 50 hours. In the other hand, measurements of Cu-CeYSZ electrodes showed that the resistance reduces over time in dry methane. Measurements in wet (~3 % H_2O) methane revealed that the resistance of both electrodes reduces considerably, even by a factor of 40. Even though the results clearly show a strong dependence of the material's performance with the humidity of the atmosphere, the role played by cerium during the oxidation of methane is not yet understood.

Vasiliki et al. [3] have previously studied the role played by Ce in Ni-GDC (gadolinium-doped ceria) anodes using NEXAF measurements combined with transient chronoamperometric experiments and DFT calculations. Vasiliki et al. tracked the Ce^{3+}/Ce^{4+} ratio over time in presence of H_2 and methane, determining the optimal condition of operation of this anode. Other studies of the cerium oxide state in cerium oxide surfaces have been done by Mullins et al. [4]. In this work we discuss the chance to apply X-ray Absorption Spectroscopy (XAS) techniques to study the role played by Ce^{3+}/Ce^{4+} ions in the electro-catalytic activity of Cu-CeYSZ and Cu-CeO_2-CeYSZ anodes working in different atmosphere conditions: H_2, CH_4 and CH_4+H_2O. These measurements would give an insight to determine the role of Ce inside the YSZ structure or in the CeO_2 nanoparticles in the electrocatalytic process and help determine whether or not Ce reduction improves the anode performance.

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