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Doping effect on the hydrogen production via microwave assisted water splitting in doped-ceria materials.

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Nowadays, hydrogen is being used as an energetic vector for saving excess of renewable energy. The most used techniques to generate hydrogen are thermochemical looping's, electrolysers and hydrocarbons reforming. However, all these techniques have several drawbacks, namely the high temperatures needed, the use of sophisticated machinery and the long operation times required for the hydrogen production. Recently, the possibility to generate green hydrogen using electric energy, as microwave radiation, has been reported. This process uses metallic oxides as catalysts, e.g. CeO₂, and it occurs in a reactor at temperatures lower than 250 °C in less than five minutes. The hydrogen production mechanism happens in two steps. First, the material is irradiated with a microwave electromagnetic field, producing the reduction of the material with the concomitant release of oxygen. This radiation is able to stabilize a higher amount of oxygen vacancies in the fluorite structure at lower temperatures than the conventional radiative processes, as it is the case of thermosolar (>1000 °C). When the microwaves are turned off in the presence of water, the material splits the H₂O molecule, therefore liberating a stream of molecular hydrogen and filling its oxygen vacancies. One example of this process is noted in the material Ce_{0.8}Gd_{0.2}O₂. The release of oxygen is accompanied by an increase in the material electrical conductivity. Besides, it has been observed that a different conductivity behaviour can be inferred depending on the irradiated microwave power. If the microwave radiation power is lower than the activation energy (P_{Th}), the material conductivity behaves like conventional heating process. On the other hand, for a microwave radiation power higher than the P_{Th} , the material undergoes a sudden spike in the conductivity. This rise is mainly ascribed to an increase of the electronic conductivity. Ionic conductivity can be tuned by doping the ceria lattice with iso and aliovalent cations. For example, incorporating Zr into the structure, the ionic conductivity decreases, while Gd generates oxygen vacancies in the anionic sublattice, thus, increasing the ionic conductivity. In this work, we have synthesized and characterized a set of ceria doped materials, e.g. Ce_{1-x}M_xO (M = La, Y, Yb, Tb, Zr, and Gd) (x = 0.1 and 0.2). Their interaction with microwave radiation has been monitored to study their modulability regarding conductivity behaviour and hydrogen production capacity.

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