

In attempting to understand the enhanced proton conductivity of the modified PBI membrane despite its lower acid content, by nearly a factor of two, we performed  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  nuclear magnetic resonance (NMR) measurements. Proton self-diffusion coefficients for membranes prepared by the modified process and by the original PPA process, were measured by pulsed field gradient NMR.

The results show significantly enhanced proton diffusivity, both in magnitude and in lower activation energy for the dense and re-acidified membrane, which is consistent with its high conductivity despite lower acid content compared to the original PPA-processed membranes. We have also performed solid state magic angle spinning cross-polarization one-dimensional  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{31}\text{P}\{^1\text{H}\}$  and two-dimensional  $^{31}\text{P}\{^1\text{H}\}$  and  $^{13}\text{C}\{^1\text{H}\}$  HETCOR NMR measurements, which yield additional information on structural differences between the membranes and how these differences may affect transport properties. In particular, the results demonstrate a more rigid glassy structure of the polymer and stronger coupling between phosphate moieties and the polymer backbone in the modified membrane, which may enhance proton transport via the Grothuss mechanism.

1. Multinuclear NMR Study of the Effect of Acid Concentration on Ion Transport in Phosphoric Acid Doped Polybenzimidazole Membranes, S.N. Suarez, N.K.A.C. Kодиweera, P. Stallworth, S.G. Greenbaum, S. Yu, and B. Benicewicz, *Journal of Physical Chemistry B*, 116, 12545-51(2012).

#### EF10.16

**Tuning of Shape, Disorder and Oxygen Vacancies in Lanthanum-Doped (0-70%) Ceria Shaped Nanoparticles for Oxidative Coupling of Methane** Fabiane d. Trindade<sup>1</sup>, Sergio Damasceno<sup>1</sup>, Larissa Otubo<sup>2</sup>, Daniel Z. Florio<sup>1</sup>, Fabio Fonseca<sup>2</sup> and Andre S. Ferlauto<sup>1</sup>; <sup>1</sup>Universidade Federal do ABC, Brazil; <sup>2</sup>Instituto de Pesquisas Energeticas e Nucleares, Brazil

The abundance of natural gas due to the advancements in exploration and extraction has increased the interest in the direct conversion of methane to  $\text{C}_2$  molecules via oxidative coupling of methane (OCM) reactions. However, the achievement of viable catalytic routes for such reactions has been a challenge due to thermodynamic limitations. In this work, we investigate lanthanum doped cerium oxide nanoparticles as catalysts for OCM. La was chosen due to its 3+ valence, which results in the formation of oxygen defect sites in Ce:La solid solutions, and to its high thermal stability and basicity. The fine-tuning of the size, shape and defects of cerium-lanthanum oxide nanoparticles was achieved by varying La concentration and synthesis temperature.  $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$  nanoparticles having  $\text{La}^{3+}$  concentration,  $x$ , varying between 0 and 70 mol% were synthesized via a template-free hydrothermal process. Two series of samples were investigated using a hydrothermal temperature of 110 °C (nanorods) to 180 °C (nanocubes) and keeping all other synthesis parameters equal. The morphology of the  $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$  NPs was determined by scanning electron microscopy (SEM) and high-resolution electron microscopy (HRTEM). The SEM and TEM images reveal that  $\text{La}^{3+}$  addition significantly impacts the morphology of the obtained  $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$ -110 °C and  $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$ -180 °C nanostructures. As the  $\text{La}^{3+}$  doping increases, the rods and cubes organize themselves in an oriented attachment mechanism. X-ray diffraction analysis indicates that, upon doping ceria with  $\text{La}^{3+}$ , no separate peaks corresponding to  $\text{La}_2\text{O}_3$  are observed for  $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$ -110 °C for  $x < 0.7$ . The incorporation of  $\text{La}^{3+}$  into the  $\text{CeO}_2$  crystal structure results in an expansion of the fluorite lattice. On the other hand, for the  $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$ -110 °C, for  $\text{La}^{3+}$  content  $x > 0.40$ , extra broader reflections are observed, indicating that two fluorite phases are present which have different lattice parameters and crystallite sizes. They can be associated with two distinct morphology, cubes and rods. In addition,  $\text{La}^{3+}$  addition results in a significant increase in microstrain reflecting the large disorder of the structure associated with the difference in cations size, excess of vacancies and random distribution of cations and anions in their sublattices. Raman spectroscopy was also used to investigate the disorder and defect formation. A red-shift of the main fluorite  $\text{F}_{2g}$  peak is observed that reflects the expansion of the structure. More interestingly, as  $\text{La}^{3+}$  concentration increases, the  $\text{F}_{2g}$  broadens significantly and the formation of different amounts of extrinsic and intrinsic oxygen vacancies is revealed by the emergence of a "defect" band at 500-600  $\text{cm}^{-2}$ . Such effect is stronger in the  $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$ -110 °C series, indicating that the rod-like nanostructures prepared at lower T can accommodate a much higher level of defects and disorders.

The catalytic performance of the  $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$  NPs for the OCM reaction was evaluated in a fixed-bed reactor at 750 °C. The reagents  $\text{CH}_4$  and  $\text{O}_2$  and the products  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$ , were measured by an in-line mass spectrometer.  $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$ -110 °C ( $x = 0.5$ ) showed the best catalyst performance has 25% of methane conversion and 48% of selectivity for the formation of  $\text{C}_2$  products. By increasing  $\text{La}^{3+}$ , the selectivity to  $\text{C}_2$  hydrocarbons was increased. The correlation of Raman spectroscopy and catalysts results suggests that the high concentration of defects and/or high disorder in the  $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$ -110 °C ( $x = 0.5$ ) nanorods were crucial to improving conversion rates and selectivity.

#### EF10.17

**Doping Effect on the Hydrogen Production via Microwave Assisted Water Splitting in Doped-Ceria Materials** Aitor Domínguez<sup>1</sup>, Laura Navarrete<sup>1</sup>, Maria Balaguer<sup>1</sup>, Joaquin Santos<sup>1</sup>, Pedro José Plaza<sup>2</sup>, José Manuel Catalá<sup>2</sup> and José Manuel Serra<sup>1</sup>; <sup>1</sup>Instituto de Tecnología Química, Spain; <sup>2</sup>Institute of Information and Communication, Spain

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, electrolyzers 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.  $\text{CeO}_2$ , 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  $\text{H}_2\text{O}$  molecule, therefore liberating a stream of molecular hydrogen and filling its oxygen vacancies. One example of this process is noted in the material  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ .

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 similar to 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  $\text{Zr}^{4+}$  into the structure, the ionic conductivity decreases, while  $\text{Gd}^{3+}$  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.  $\text{Ce}_{1-x}\text{M}_x\text{O}_2$  ( $\text{M} = \text{La}, \text{Y}, \text{Yb}, \text{Tb}, \text{Zr}$ , and  $\text{Gd}$ ) ( $x = 0.1$  and  $0.2$ ). Their interaction with microwave radiation has been monitored in order to study their modulability regarding conductivity behaviour and hydrogen production capacity.

#### EF10.18

**Experiment Driven Computational Analysis of Solar Thermochemical Hydrogen Production Materials** Andrew I. Smith; Sandia National Laboratories, United States

The production and use of clean hydrogen is an important step in the decarbonization of the world's energy economy. Currently hydrogen is used in various important chemical applications and is playing an ever-increasing important role in the difficult to electrify energy markets of construction and long-haul transportation. The US currently produces ~10 million metric tons of hydrogen per year, with most of the hydrogen being produced by steam methane reforming of fossil fuels.<sup>1</sup> The desire for clean hydrogen has resulted in governments and institutions investing in clean hydrogen technologies