

Thus, under optimized conditions, it was possible to observe that ceria and zirconia oxides can efficiently promote the conversion of methane to other commercially valuable products using suitable oxidation potentials and, therefore, be a promising alternative for this reaction.

EF10.12

Effects of La Content in Ceria-Lanthana Thin Films Prepared by Pulsed Laser Deposition [Raphael A. Martins Pires de Oliveira](#)¹, Andre S. Ferlauto¹, Fabiane d. Trindade¹, Daniel Z. Florio¹ and Fabio Fonseca²; ¹Universidade Federal do ABC, Brazil; ²Instituto de Pesquisas Energeticas e Nucleares, Brazil

Solid oxide electrochemical reactors are a promising alternative for hard to tackle chemical reactions such as oxidative coupling of methane (OCM), in which methane is converted to C₂+ products. They contain oxygen-conducting membranes that deliver oxygen species in a highly controllable way, avoiding undesired complete oxidation, thus enhancing selectivity. Cerium oxide is one the main studied oxide membrane material because, when doped with 3+ rare earth cations such as Gd, Sm or La, it gains high ionic conductivity in the ideal temperature range for conversion reactions (600-900°C). Interestingly, recent works has shown that ceria-lanthana is a promising catalyst for OCM. The presented work investigates the structural properties La_xCe_(1-x)O_{2(1-x/2)} thin films covering a wide La content range from x = 0 to 0.7. The films were prepared by pulsed laser deposition on Si, quartz and glass substrates, using La_xCe_(1-x)O_{2(1-x/2)} targets with same stoichiometry. We have used x-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy and spectroscopic ellipsometry (SE) to study the effect of doping on the structural properties of the films. XRD results indicate that the film growth is textured. For low La content (x≤0.5), the films growth preferably in the [100] direction of the cubic crystalline fluorite, whereas for x>0.5 film crystalline orientation is random. La doping induces an expansion of the fluorite structure reflecting an increase in lattice parameter (from 5.42 Å, for x=0, to 5.69 Å, for x=0.7) that follows the same trend that is observed for the powders from which the PLD targets were made. The doping effects in Ce-La thin films were studied using Raman spectroscopy by following the changes in the main fluorite F_{2g} band at ~464 cm⁻¹. La doping induces a significant broadening of this peak. Such effect is usually attributed to reduced size in pure ceria nanoparticles, but in this case, it is probably associated to cationic (or anionic) disorder that exists in the so- disordered fluorite structure that is characteristic of ceria-lanthana solid solutions. The disorder results in a reduced phonon correlation length that induces the broadening. These results will pave the way for the application of Ce-La oxides thin films as catalysts for OCM in electrochemical reactors based on ceria.

EF10.13

Fabrication of Bundle-Type Columnar Cuprous Oxide Photocathodes with Vertical Grain-Boundaries by Metallic Seeds and Their Enhanced Photoelectrochemical Water Splitting Performance [Ji Hoon Choi](#), Dong Su Kim, Hak Hyeon Lee and Hyung Koun Cho; Sungkyunkwan University College of Natural Science, Korea (the Republic of)

Controlling and designing grain-boundaries (GBs), which cause recombination losses as planar defects in the absorbing layers are an essential strategy for the development of the highly efficient photoelectrochemical reaction systems. We suggest the method to design progressive bundle-type columnar structure as an alternative of single crystal with the fewest defects, where the GBs were aligned in parallel with charge transport movement and electric field direction. The instant strike bias (10 ms) in the same electrolytes induces the formation of island-shaped metallic Cu nanoparticles in the initial stage as seed crystals for controlling the Cu₂O growth evolution, and results in the dramatically high density Cu₂O nuclei and bundle-type columnar Cu₂O growth with longitudinal GBs, contrary to the typical randomly-crystallized Cu₂O. The metallic Cu seeds with stronger electric field than the exposed ITO region provide the selective crystallization sites for Cu₂O growth along the <111> ionic bonding. Despite ultimately instant strike interval, the p-type Cu₂O photoelectrodes retain outstanding photocurrent of 5.2 mA/cm² and on-set potential of 0.7 V at 0 V_{RHE}, owing to highly improved transport and transfer efficiencies inside the Cu₂O by suppressing effectively charge scattering in the GBs. Consequently, it is decisive that designing the bundle-type columnar structure could be a good strategy in developing the photocathodes with enhanced photoelectrochemical reaction.

EF10.14

Novel High Entropy Oxides for Oxygen Storage and Generation [Alicja Klimkowicz](#)^{1,2}, Shotaro Dokin¹ and Akito Takasaki¹; ¹Shibaura Kogyo Daigaku, Japan; ²Kanagawa Daigaku, Japan

Oxygen is an essential industrial gas utilized in many sectors, such as steel production. On a large scale, oxygen is produced by cryogenic distillation and used in many technologies, such as steel, paper, methanol production. However, the need for local, scattered oxygen generation for healthcare, sterilization, and wastewater treatment is rapidly growing. A small-scale oxygen generator relying on the adsorption (or absorption) method can satisfy the oxygen demand. In the Temperature Swing Absorption (TSA) method, the oxygen is absorbed at a lower temperature and released at a higher temperature, and the oxygen partial pressure remains constant. Analogously, in the Pressure Swing Absorption (PSA) method, the oxygen is absorbed into the material at a higher oxygen partial pressure over the sample and released at a lower pressure. The PSA process takes place at a constant temperature. The TSA and PSA methods rely on appropriate absorbing material, which is a device's heart. Oxygen storage materials (OSM) are used as absorbers for oxygen production using absorption methods. Naturally, the efficiency of the oxygen generation process depends on the performance of those materials. Therefore, the ideal OSM should reversibly absorb/desorb a large amount of oxygen (high δ) that translates to a high oxygen storage capacity (OSC > 3 wt. %). The oxygen absorption and desorption kinetics should be fast; the operating temperature should be below 400 °C. Currently, there is no material that meets all the requirements. Therefore, a search for new OSMs is ongoing. A new group of materials, high entropy oxides (HEO), is proposed as potential OSM absorbers. The HEOs are defined as multi-elemental compounds in equimolar or near-equimolar ratios stabilized in a simple solid solution structure due to the high configurational entropy. In 2015, Rost et al. synthesized the first entropy-stabilized oxide (Mg-Ni-Co-Cu-Zn)O. In 2017, Sarkar et al. examined the formation of high entropy oxides and showed that using theoretical calculations, HEO can exhibit high oxygen vacancies (δ). The calculated oxygen vacancies (δ) increase with the number of cations in HEOs, and it can be as high as $\delta = 0.38$ for (CeLaPrSmY)O_{2- δ} resulting in a 3.54 theoretical OSC. The HEOs look very promising since a high and reversible oxygen content change is a prerequisite for good OSMs. In this research, the sinterability of the (nLn_{1/n})O_{2- δ} (where Ln = Lanthanides, n = 4, 5, 6, 7) high entropy materials will be confirmed. The crystal structure of the multi-elemental compounds will be investigated. The amount of oxygen vacancies will be studied together with oxygen storage and generation properties of novel high entropy oxides.

EF10.15

NMR Investigation of Proton Transport in Mechanically Robust Polybenzimidazole/Polyphosphoric Acid Membranes [Laura Murdock](#)¹, [Tawhid Pranto](#)², [Mounesha Garaga](#)³, [Sophia Suarez](#)⁴, [Brian Benicewicz](#)¹ and [Steve Greenbaum](#)³; ¹University of South Carolina, United States; ²CUNY The Graduate Center, United States; ³Hunter College of CUNY, United States; ⁴Brooklyn College, United States

Previous work by some of us has demonstrated enhanced electrochemical performance of polybenzimidazole (PBI) membranes with high phosphoric acid content prepared by the so-called PPA process.¹ We report here a new synthetic route to dense PBI films, with repeat unit para-PBI and without the use of any organic solvents, which were originally developed for flow battery applications. However these films also can be re-doped in phosphoric acid to be used as membranes in high-temperature PEM fuel cells. The re-doped PBI films display high ionic conductivity at elevated temperatures, similar to the starting PBI gel membranes prepared by the PPA process¹, while also exhibiting enhanced mechanical properties. Thus, in high-temperature PEM fuel cell operation the electrochemical performance is similar, but performance degradation due to mechanical creep is reduced, leading to greater durability of the modified and re-acidified PBI membrane.