

Protonic Conductivity Highlighted by Impedance Measurement of Y-Doped BaZrO₃ Synthesized by Supercritical Hydrothermal Process

Authors : Melanie Francois, Gilles Caboche, Frederic Demoisson, Francois Maeght, Maria Paola Carpanese, Lionel Combemale, Pascal Briois

Abstract : Finding new clean, and efficient way for energy production is one of the actual global challenges. Advances in fuel cell technology have shown that, for few years, Protonic Ceramic Fuel Cell (PCFC) has attracted much attention in the field of new hydrogen energy thanks to their lower working temperature, possible higher efficiency, and better durability than classical SOFC. On the contrary of SOFC, where O²⁻ oxygen ion is the charge carrier, PCFC works with H⁺ proton as a charge carrier. Consequently, the lower activation energy of proton diffusion compared to the one of oxygen ion explains those benefits and allows PCFC to work in the 400-600°C temperature range. Doped-BaCeO₃ is currently the most chosen material for this application because of its high protonic conductivity; for example, BaCe_{0.9}Y_{0.1}O_{3-δ} exhibits a total conductivity of 1.5×10⁻² S.cm⁻¹ at 600°C in wet H₂. However, BaCeO₃ based perovskite has low stability in H₂O and/or CO₂ containing atmosphere, which limits their practical application. On the contrary, BaZrO₃ based perovskite exhibits good chemical stability but lower total conductivity than BaCeO₃ due to its larger grain boundary resistance. By substituting zirconium with 20% of yttrium, it is possible to achieve a total conductivity of 2.5×10⁻² S.cm⁻¹ at 600°C in wet H₂. However, the high refractory property of BaZr_{0.8}Y_{0.2}O_{3-δ} (noted BZY20) causes problems to obtain a dense membrane with large grains. Thereby, using a synthesis process that gives fine particles could allow better sinterability and thus decrease the number of grain boundaries leading to a higher total conductivity. In this work, BaZr_{0.8}Y_{0.2}O_{3-δ} have been synthesized by classical batch hydrothermal device and by a continuous hydrothermal device developed at ICB laboratory. The two variants of this process are able to work in supercritical conditions, leading to the formation of nanoparticles, which could be sintered at a lower temperature. The as-synthesized powder exhibits the right composition for the perovskite phase, impurities such as BaCO₃ and YO-OH were detected at very low concentration. Microstructural investigation and densification rate measurement showed that the addition of 1 wt% of ZnO as sintering aid and a sintering at 1550°C for 5 hours give high densified electrolyte material. Furthermore, it is necessary to heat the synthesized powder prior to the sintering to prevent the formation of secondary phases. It is assumed that this thermal treatment homogenizes the crystal structure of the powder and reduces the number of defects into the bulk grains. Electrochemical impedance spectroscopy investigations in various atmospheres and a large range of temperature (200-700°C) were then performed on sintered samples, and the protonic conductivity of BZY20 has been highlighted. Further experiments on half-cell, NiO-BZY20 as anode and BZY20 as electrolyte, are in progress.

Keywords : hydrothermal synthesis, impedance measurement, Y-doped BaZrO₃, proton conductor

Conference Title : ICBFCT 2020 : International Conference on Battery and Fuel Cell Technology

Conference Location : Rome, Italy

Conference Dates : September 17-18, 2020