The Serbian Society for Ceramic Materials

Institute for Multidisciplinary Research, University of Belgrade

Institute of Physics, University of Belgrade

Center of Excellence for the Synthesis, Processing and Characterization of Materials for use in Extreme Conditions "CEXTREME LAB" - Institute of Nuclear Sciences "Vinča", University of Belgrade

Faculty of Mechanical Engineering, University of Belgrade

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Branko Matović
Zorica Branković
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I-25

IMPROVED PROPERTIES OF DOPED $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ AS A PROTON CONDUCTING ELECTROLYTE FOR IT-SOFC

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The proton conductivity is an exclusive property of mixed oxides with perovskite structure and large unit cell volume, such as $BaCeO_3$ or $SrCeO_3$. Doping with aliovalent cations (Y^{3+}) that replace Ce^{4+} induces formation of point defects (oxygen vacancies), which in wet or hydrogen containing atmosphere produce proton defects highly mobile at elevated temperatures. $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ (BCY) is one of the best proton conducting electrolyte at temperatures between 500 and 700 ºC, which allows its application in intermediate-temperature solid oxide fuel cells (IT-SOFC). Yet, one of the main drawbacks of this material is its instability in CO_2-rich atmospheres. Since BCY is basic in character, it normally reacts with CO_2 to form $BaCO_3$ and yttria doped ceria. Both products exhibit no proton conductivity, thus limiting application of BCY in IT-SOFCs where CO_2 appears as a product of electrochemical performance. However, the stability of BCY can be improved by doping with cations that may raise the acidic character of the material, such as Nb^{5+}, Ta^{5+} or In^{3+}. Introduction of Nb^{5+} and Ta^{5+} will reduce the amount of point defects and consequently decrease the proton conductivity. This relation has been known as trade-off effect. Nevertheless, if their molar concentration exceed no more than 5% it is possible to obtain functional electrolytes with satisfying stability and conductivity. On the other hand, trivalent In^{3+} can completely replace Y^{3+} since it can both serve as a point defect source and increase acidity of the crystal lattice. Accordingly, it can be introduced in much larger amounts than Nb^{5+} or Ta^{5+}.

In this study $BaCe_{0.9-x}Nb_xY_{0.1}O_{3-\delta}$ (where x = 0.01, 0.03 and 0.05) and $BaCe_{1-x}In_xO_{3-\delta}$ (where x = 0.15, 0.20 and 0.25) powders were synthesized by the method of autocombustion, while $BaCe_{0.9-x}Ta_xY_{0.1}O_{3-\delta}$ (where x = 0.01, 0.03 and 0.05) powders were prepared by the classical solid state route. Much higher specific surface areas were observed for the samples synthesized by the autocombustion method. In the case of the samples doped with Nb and Ta, the dense electrolytes were formed after sintering at 1550 ºC for 5 h in air. Temperature of 1300 °C was enough to complete sintering of the samples doped with In after 5 h in air, which was another advantage of In as a dopant. The conductivities determined by impedance measurements in temperature range of 550–700 °C in wet hydrogen showed a decreasing trend with increase of Nb and Ta content, while it was the opposite in the case of In. Interestingly, the total conductivity of $BaCe_{0.85}Nb_{0.05}Y_{0.1}O_{3-\delta}$, $BaCe_{0.85}Ta_{0.05}Y_{0.1}O_{3-\delta}$ and $BaCe_{0.75}In_{0.25}O_{3-\delta}$ reached around 5×10^{-3} S/cm in wet hydrogen atmosphere at 700 °C. After exposure in 100 % CO_2

atmosphere at 700 °C for 5 h, the samples were investigated by X-ray analysis. It was found that even 15 % In could completely supress degradation of the electrolyte, while the highest concentrations of Nb and Ta (5%) were necessary to secure sufficient stability in CO_2.

O-1

SYNTHESIS AND CHARACTERIZATION OF ZINC DOPED COBALT FERRITE NANOPARTICLES

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In the last two decades spinel ferrites nanoparticles have been one of the most versatile system due to their potential applications in a wide variety of fields such as data storage, catalysis, environment, and especially biomedicine. Among them, cobalt ferrite ($CoFe_2O_4$, CFO) is material with the large magnetocrystalline anisotropy and high magnetization; also it shows good chemical and thermal stability and good mechanical properties.

In the present work, a set of zinc doped CFO nanoparticles with different amounts of zinc ions ($Co_{1-x}Zn_xFe_2O_4$; x=0, 0.05, 0.1, 0.3 and 0.5) but with the same particles size, particles size distribution and capping agent were prepared by solvothermal synthesis method. The obtained samples were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR) and superconducting quantum interference device (SQUID). The XRD patterns show the common Bragg peaks typical of a cubic spinel structure (PDF card 22-1086) for all the samples. No other phases are detected. TEM analysis confirms the presence of sphere-like particles with equal mean diameter for all the samples ($<D_{TEM}>$ = 5 nm). The FT-IR analysis confirms the presence of oleic acid on the surface of the nanoparticles and revealed that oleic acid forms covalent bidentate with metal ions on the particle surface. Preliminary magnetization measurements has been done on all the samples. Field dependence of magnetization recorded at low temperature 5 K show an hysteretic behavior with increase of coercive field with decrease of zinc content (Hc(CFO)=1.13 T; H_C(CoZn_x_0.3)=0.81 T).