

論文内容要旨

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学位論文題目	Structure changes of $Ce_{1-x}Ln_xO_{2-\delta}$ ($Ln = La, Gd$) and $Ba_{1-x}Zr_{1-y}Y_yO_{3-\delta}$ solid electrolytes (La及びGdドープ酸化セリウム及びYドープジルコニウム酸バリウムの構造変化)		
<p>内容要旨</p> <p>As entering in the 21st century, energy and the environment issues are putting more and more pressure on human beings, and the call for improving the living environment of human beings as soon as possible is getting higher and higher. As a new, efficient and clean energy source, fuel cell power generation technology has attracted widespread attention of the world.</p> <p>Minimum assembly of fuel cells are composed of three major parts; a cathode, an anode and an electrolyte. Air is supplied to the cathode and fuel is supplied to the anode (in this case H_2) which is oxidized releasing electrons. Electrons pass to the cathode where they reduce the oxygen at the electrode/electrolyte interface.</p> <p>According to different types of electrolytes, the fuel cells can be divided into five categories: alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFCs), and molten carbonate fuel cells (molten carbonate fuel cells). MCFC), solid oxide fuel cell (SOFC), proton exchange membrane fuel cell (PEM FC). Among them, high-temperature solid oxide fuel cells (SOFC) have all-solid structure and higher energy. The outstanding characteristics such as efficiency and wide adaptability to various fuel gases such as gas, natural gas and mixed gas are the fastest, and the above characteristics are also the basis for its wide applications.</p> <p>According to a previous report, the electrical conductivity is related with the calcined temperature. Otherwise, the electrical conductivity of $Ce_{1-x}La_xO_{2-\delta}$ (LDC) shows a specific behavior at $x = 0.3$. Thus, we suspect that a local structural change also occurred in our target materials. $BaCeO_3$ has low chemical stability under CO_2 and H_2O atmospheres. In contrast, $BaZrO_3$ has excellent chemical stability. However, high sintering temperature and long sintering duration are required to obtain a high density $BaZrO_3$ material. Therefore, in order to obtain a high density sample, a sintering aid such as ZnO or CuO would be required.</p> <p>In the first part of work, we synthesis the $Ce_{1-x}La_xO_{2-\delta}$ ($x=0.1-0.5$) samples with the co-precipitation method. We research about the starting conditions about the ratio between metal ion and precipitating reagent are 1:20, 1:15 and 1:5, respectively. We can conclude from the measurement results that the particle size of the calcined particles is related with the starting material concentration and the best conditions are 1:15 about the ratio of metal ion and precipitating reagent. Then we synthesis the $Ce_{1-x}La_xO_{2-\delta}$ ($x = 0.1- 0.5$) samples under this condition. When we calculated</p>			

the lattice parameters of each sample, the experimental data is not fit with the theoretical one. So we suspect that there is a structure change at $x=0.3$ of $Ce_{1-x}La_xO_{2-\delta}$ ($x = 0.1-0.5$) samples.

In the second part of work, the changes in local structures of $Ce_{1-x}Ln_xO_{2-\delta}$ with Ln (La, Gd) doping were investigated. XAFS was successfully used to clarify the coordination environments around Ce and the dopant La and Gd. For LDC, La coordination was maintained at 7, and Ce coordination decreased from 8 to 6. It was speculated that because a superstructure would be formed which was more like a pyrochlore structure in LDC at $x>0.3$, the oxygen vacancies could be attracted by the larger La^{3+} . For GDC, the coordination numbers for Gd and Ce decreased from 8 to 6. In the GDC, oxygen vacancies had no preference for Ce or Gd coordination. We also combined XRD results and EXAFS results together. These results explained the changes in the lattice parameters for both LDC and GDC. The local structure change model was designed and the electric conductivity change at each stage of Ln (La, Gd) doping was explained. In future studies, these results can be applied to other materials.

In the third part of work, we synthesis the $Ba_{1-x}Zr_{1-y}Y_yO_{3-\delta}$ ($x = 0.02, 0.04$) and ($y = 0.1, 0.2, 0.3$) samples successfully and researched about the experiment conditions with XRD measurement. It is confirmed that the $Ba_{0.96}Zr_{0.9}Y_{0.1}O_{3-\delta}$ is the best condition. Then we add the ZnO as the sintering aid to obtain the $Ba_{0.96}Zr_{0.9}Y_{0.1}O_{3-\delta} + ZnO$ (0-3wt%) samples sintered at 1500 °C for 5h. As a result, the relative density could reach 99.6% of $Ba_{0.96}Zr_{0.9}Y_{0.1}O_{3-\delta} + ZnO$ 3wt%. And the electrical conductivity of $Ba_{0.96}Zr_{0.9}Y_{0.1}O_{3-\delta} + ZnO$ 1 wt% sample was the highest. It was considered that the reason was the perovskite structure was destroyed so that the grain boundary resistance was increased. Then we tried to prevent BaO pellet sublimation and surface decomposition with powder bed method. It was thought that ZnO was amorphous or existed between lattices. From EDS result, it was found that Y precipitation on the pellet surface could be suppressed by the PB method. It is hoped that powder bed method could prevent the BaO pellet sublimation and surface decomposition in the future work.