論文 / 著書情報
Article / Book Information

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著者(和文)	MUHAMMADIQBAL
Author(English)	Muhammad Iqbal
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博士課程)
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論文要旨

THESIS SUMMARY

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学籍番号： Student ID Number		指導教員（主）： Academic Advisor(main)	Prof. Ryoji Kanno
学生氏名： Student's Name	Muhammad Iqbal	指導教員（副）： Academic Advisor(sub)	Dr. Hirayama Masaaki

要旨（英文 800 語程度）
Thesis Summary (approx.800 English Words)

The aim of this thesis is mainly synthesizing new materials and investigating their physical properties for the better oxide ionic conduction than the existing solid oxide electrolyte materials for sold oxide fuel cells.

Solid oxide fuel cells (SOFCs) are highly promising energy converting devices with four times better efficiency than internal combustion engines. However, the key issue related to SOFC is high operating temperature, resulting in higher systems costs and performance degradation with time. The component that is responsible of high temperature operation is solid electrolyte, an oxide ion conductor. There is very strong appeal to discover new oxide ion conductors to fabricate SOFCs at lower temperature. The oxide ionic conduction is either based on vacancy conduction or intestinal ionic conduction routes. New vision of oxide ionic conduction, inducing oxide vacancies as well as interstitials defects in same structure, can enhance the oxide diffusion properties. However, there is little previous work regarding the systems having oxide vacancies and interstitial simultaneously. Layered structured materials have the potential to sustain both kind of defect in their crystalline systems. There are wide verities of transition metal free layered oxides but among them rare earth oxycarbonate and Ruddlesden–Popper type K_2NiF_4 are of particular interest. They are wide range flexible crystalline structure to introduce vacancies and interstitial to oxygen sub-lattice, which can actively enhance the high oxygen diffusion rate in the solid materials.

An oxide ion conductor, $La_2Li_{2x}(CO_3)_{1-x}O_{2+x}$ ($x = 0.15$) has been synthesized using a solid-state reaction method. This material exhibits a conductivity of 5.5×10^{-5} S cm^{-1} at 450 °C. Detailed Rietveld analysis of the synchrotron X-ray and neutron diffraction data, demonstrated that the insertion of lithium into the structure leads to loss of $(CO)^{2+}$ units and also to displacement of carbon and oxygen atoms from their original positions in the parent structure. These structural changes create oxygen vacancies and also introduce interstitial oxygen in carbonate layer. Oxide vacancies and interstitial associated with carbonate anions appear to be responsible for the ionic conduction observed in this material.

A novel oxide ion conducting layered perovskite $La_2LiO_{3.5}$ has been synthesized by high-pressure solid-state reaction method. Structure of powdered sample was determined by Rietveld refinement analysis using synchrotron x-ray, neutron diffraction data. $La_2LiO_{3.5}$ has the K_2NiF_4 type structure in Ruddlesden–Popper series, an orthorhombic lattice with space group *Fmmm*. During the refinement, the oxygen vacancies have been observed at axial position of LiO_6 octahedra and they seams to be responsible of oxide diffusion in $La_2LiO_{3.5}$ structure. However, the significantly large Li-O2 bond length (2.37 Å) than the sum of the respective ionic radii (2.16 Å) assist in creating the conduction pathway along the intestinal oxygen O3 sites through the LaO rock salt layers. The observed conductivity value for the sample is 2.68 x 10^{-4} Scm^{-1} (E_a = 106.3 kJ/mol) at 358 °C (Figure 2) that is the highest yet reported value for known perovskite solutions at this temperature. The conductivity enhancement is interpreted as being due to the presence of oxygen vacancies along with interstitial sites in in the structure.

The effect of cation doping at different sites of $La_2LiO_{3.5}$ was also investigated. Solid solutions $La_{2-x}Ce_xO_{3.5+x/2}$ (x = 0.1) and $La_2Li_{1-x}Mg_xO_{3.5+x/2}$ (x = 0.1 x = 0.2) were successfully synthesized using a high-pressure solid-state reaction method. Parent material has $La_2LiO_{3.5}$ has orthorhombic (*Fmmm*) base structure. This structure model retain its geometry with Ce^{+4} substitution ($La_{2-x}Ce_xO_{3.5+x/2}$) range of x < 0.1. $La_{2-x}Ce_xO_{3.5+x/2}$ (x = 0.1) does not show better conductive properties. On the other hand Mg^{+2} substitution at Li^+ site, has remarkable effect on the structure as well as properties of $La_2LiO_{3.5}$ material.

Phase transition, from orthorhombic (*Fmmm*) to tetragonal (*I4/mmm*), has been observed even very small amount of Mg cation doping at Li sub lattice. Structural data, based on synchrotron X-ray diffraction analysis, indicate an increase in the value of O1 occupation parameter from 0.70 (in $La_2LiO_{3.5}$) to 0.73 in $La_2Li_{0.9}Mg_{0.1}O_{3.55}$ might be the main reason for the better ionic conductivity in this structure. During the refinement most oxide defect appears at axial oxygen in the LiO_6 octahedra these oxide vacancies involved in conduction via vacancy conduction pathway. The apical oxygen can contribute in conduction while because they have strong co-relation with interstitial oxygen. The highest conductivity was obtained at the composition of $La_2Li_{1-x}Mg_xO_{3.5+x/2}$ (x = 0.1) with the conductivity value of 2.41 x 10^{-4} S cm^{-1}. Enhanced ionic conductivity in Mg doped sample is considered to be higher oxygen contents (less vacancy ordering) in $La_2LiO_{3.5}$ material. The idea of having interstitial and vacancies in a same structure has been first time investigated in this study.

備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 2 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 2 copies of 800 Words (English).