

論文 / 著書情報  
Article / Book Information

題目(和文)	
Title(English)	Synthesis, structure, and electrochemical properties of ion conductive oxides with layered oxycarbonate and K <sub>2</sub> NiF <sub>4</sub> structures
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出典(和文)	学位:博士(理学), 学位授与機関:東京工業大学, 報告番号:甲第9259号, 授与年月日:2013年9月25日, 学位の種別:課程博士, 審査員:菅野 了次,大坂 武男,川路 均,中村 二郎,平山 雅章
Citation(English)	Degree:Doctor (Science), Conferring organization: Tokyo Institute of Technology, Report number:甲第9259号, Conferred date:2013/9/25, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

## Synthesis, Structure and Electrochemical Properties of Ion Conductive Oxides with Layered Oxycarbonate and $K_2NiF_4$ Structures

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 solid 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 interstitial ionic conduction routes. New vision of oxide ionic conduction, inducing oxide vacancies as well as interstitial 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 varieties 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  $5.5 \times 10^{-5} \text{ S cm}^{-1}$  at  $450 \text{ }^\circ\text{C}$ . 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 seem to be responsible of oxide diffusion in  $La_2LiO_{3.5}$  structure. However, the significantly large Li-O2 bond length ( $2.37 \text{ \AA}$ ) than the sum of the respective ionic radii ( $2.16 \text{ \AA}$ ) assist in creating the conduction pathway along the interstitial oxygen O3 sites through the LaO rock salt layers. The observed conductivity value for the sample is  $2.68 \times 10^{-4} \text{ Scm}^{-1}$  ( $E_a = 106.3 \text{ kJ/mol}$ ) at  $358 \text{ }^\circ\text{C}$  (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 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  $\text{Mg}^{+2}$  substitution at  $\text{Li}^+$  site, has remarkable effect on the structure as well as properties of  $\text{La}_2\text{LiO}_{3.5}$  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  $\text{La}_2\text{LiO}_{3.5}$ ) to 0.73 in  $\text{La}_2\text{Li}_{0.9}\text{Mg}_{0.1}\text{O}_{3.55}$  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  $\text{LiO}_6$  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  $\text{La}_2\text{Li}_{1-x}\text{Mg}_x\text{O}_{3.5+x/2}$  ( $x = 0.1$ ) with the conductivity value of  $2.41 \times 10^{-4} \text{ S cm}^{-1}$ . Enhanced ionic conductivity in Mg doped sample is considered to be higher oxygen contents (less vacancy ordering) in  $\text{La}_2\text{LiO}_{3.5}$  material. The idea of having interstitial and vacancies in a same structure has been first time investigated.

In this study mainly following results have been concluded.

1. The oxycarbonate,  $\text{La}_2\text{Li}_{2x}(\text{CO}_3)_{1-x}\text{O}_{2+x}$ , with the layered structure has been synthesized and found to exhibit a conductivity of  $5.5 \times 10^{-5} \text{ S cm}^{-1}$  at  $450^\circ\text{C}$ . Oxygen vacancies and interstitial oxygen induced by lithium insertion in the structure are responsible for the ionic diffusion.
2. A new member of Ruddlesden–Popper type structure,  $\text{La}_2\text{LiO}_{3.5}$ , has been synthesized and found to have the highest conductivity value of  $2.68 \times 10^{-4} \text{ Scm}^{-1}$  at  $358^\circ\text{C}$  with activation energy of  $106.3 \text{ kJmol}^{-1}$  among the related perovskite materials.
3. The solid solutions,  $\text{La}_{2-x}\text{Ce}_x\text{LiO}_{3.5+x/2}$  and  $\text{La}_2\text{Li}_{1-x}\text{Mg}_x\text{O}_{3.5+x/2}$ , have been synthesized and their conductivity values were clarified. Phase transition has been observed, from orthorhombic to tetragonal, by Mg doping at Li sublattice. Enhanced ionic conductivity in Mg doped sample is considered to be higher oxygen contents (less vacancy ordering) in  $\text{La}_2\text{LiO}_{3.5}$  material.

In this research we have first time investigated oxycarbonate material, and introduce a new member of Ruddlesden–Popper type material with excellent conductive properties. This research of novel  $\text{La}_2\text{LiO}_{3.5}$  material is a contribution, not only to material science but also an introduction of a new vision of oxide ion conductors. This will open a new horizon of research in layered perovskite material.