論文 / 著書情報
Article / Book Information

題目(和文)	アニオン過剰蛍石型金属水素化物のヒドリドイオン伝導
Title(English)	Hydride Ion Conduction in Anion-Excess Fluorite-Type Metal Hydrides
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第11780号, 授与年月日:2022年3月26日, 学位の種別:課程博士, 審査員:細野 秀雄,川路 均,大場 史康,神谷 利夫,松石 聡,北野 政明
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第11780号, Conferred date:2022/3/26, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	材料 系 材料 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of （ 工学 ）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

The most familiar and fundamental element, hydrogen, has been utilized as a starting material in chemical industry, and recently it attracts much attentions as a next-generation energy storage replacing fossil fuels. Especially, hydride ion (H^-) is a promising candidate for an active species in chemical reactions and energy storage systems because of its high reactivity and large redox potential. To utilize H^- for applications such as batteries, fuel cells, and electrosynthesis, development of H^- conductors is highly required. In this thesis, new H^- conductors derived from rare-earth hydrides with anion-excess fluorite structure were reported and their conduction properties were investigated. The contents in this thesis are listed below:

Chapter 1: Characteristic properties of H^-, the research background of H^- diffusion in solids, and objectives of this thesis were outlined.

Chapter 2: The pressure–chemical composition phase diagram of the LaHO–LaH_3 system was investigated. The sample at $x = 0$ crystallizes in a distorted fluorite structure with a monoclinic symmetry. For $0 < x \leq 1$, the fluorite lattice is maintained while H^- and O^{2-} ions are disordered at the regular anion position of fluorite, and an excess H^- is distributed at the interstitial site. Comparing the phase diagram and crystal structure with those of the La–F–O, Y–H–O, and Y–F–O systems, we found that the large radius ratio of cations and anions in $LaH_{1+2x}O_{1-x}$ alleviates the intrinsic Coulomb repulsion between the anions at regular positions in fluorite and the interstitial atoms. This is crucial in stabilizing the anion-excess fluorite structure without forming defect clustering and enabling fast anion conduction. These results provided guidelines for avoiding cluster formation and achieving higher conductivity in the fluorite structure.

Chapter 3: Characteristic H^- conduction of oxygen-doped LaH_3 ($LaH_{3-2x}O_x$), i.e., fast ionic conduction controlled by a pre-exponential factor was investigated. $LaH_{3-2x}O_x$ has an optimum ionic conductivity of 2.6×10^{-2} S cm^{-1} — the highest conductivity reported to date among H^- conductors at intermediate temperatures. With increasing oxygen content, the relatively high activation energy remains unchanged, whereas the pre-exponential factor decreases dramatically. This extraordinarily large pre-exponential factor is explained by introducing the temperature-dependent enthalpy, derived from H^- trapped by lanthanum ions bonded to oxygen ions. Consequently, light mass and large polarizability of H^-, and the framework comprising densely packed H^- in $LaH_{3-2x}O_x$ are crucial factors that impose significant temperature dependence on the potential energy and implement characteristic fast H^- conduction.

Chapter 4: In lightly oxygen-doped lanthanum hydride $LaH_{3-2x}O_x$ with $x < 0.25$, a H^- conductivity of ~1 mS cm^{-1} at room temperature, which is higher by 3 orders of magnitude than that of the best conductor, was reported. The oxygen concentration (x) is crucial in achieving fast H^- conduction near room temperature; the low activation barrier of 0.3–0.4 eV is attained for $x < 0.25$, above which it increases to 1.2–1.3 eV. The large-scale molecular dynamics simulations using density functional theory based neural network potential reveal that substituted oxygen ions immobilize adjacent H^-, whereas, H^- in the oxygen-free region exhibit high diffusivity with a cooperative H^- migration. These findings suggest when electronic conduction is suppressed by the minimal amount of O^{2-} substitution, the electronic conductive rare-earth hydrides can be the parent materials for fast H^- conductors.

Chapter 5: The structural and electrical characterizations of solid solution phases in LaH_3–CaH_2 and YH_3–MgH_2 were performed. In both systems, solid solution phases with anion-excess fluorite-type structure were formed. These phases exhibited relatively high ionic conductivity with low electronic conductivity (e.g. 0.19 mS cm^{-1} and 2.2 μS cm^{-1} for $La_{0.75}Ca_{0.25}H_{2.75}$ at 24°C, respectively). This result indicates that the cation substitution for $REH_{3-\delta}$ also suppress the electronic conduction similarly to the oxygen substitution for H^-. Comparing to the H^- conductivity in $La_{1-x}Ca_xH_{3-x}$, $Y_{0.67}Mg_{0.33}H_{2.67}$, $LaH_{3-2y}O_y$, $CaF_{1.06}H_{0.94}$, and CaH_2, the anion-excess fluorite structure is distinctly favorable for H^- conduction. This finding indicates that the elucidation of the origin of high hydrogen diffusivity in LaH_3 is essential to develop high-performance H^- conductors.