先端科学技術研究科　博士論文要旨

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題目	Development of novel composite solid electrolytes and fabrication of oxide-based all-solid-state batteries at room temperature 新規複合固体電解質の開発と常温成形による酸化物系全固体電池の構築		

The oxide-based solid electrolytes are critical to improving the safety of all solid-state lithium-ion batteries. Garnet-type crystalline LLZ is one of the oxide-based electrolytes that have reported to have high ionic conductivity (10^{-4} S cm^{-1}) at room temperature. However, the utilization of LLZ as an electrolyte in all-solid-state batteries has not yet been made practical. This can be accounted for LLZ particles not deforming by only the cold-pressing process. That is, LLZ particles are tough and form point contact, which results in a narrow ionic conduction path and high grain boundary resistance. The high-temperature sintering at approximately 1200 °C is required to reduce these grain boundaries between the electrolyte particles. More research is needed to reduce the sintering temperature and molding pressure for the practical application of oxide-based all-solid-state batteries. Recently, lithium-rich antiperovskite (LiRAPs: $Li_{3-x}OH_xX$ (X = Cl, Br), including x = 0) were developed as electrolytes with melting temperature of less than 300°C. The electrolytes are expected deformable.

Here, I proposed the sintering-free approach to the wide ionic conduction path by combining the LiRAPs as a soft SE and LLZs as a highly conductive hard SE. I study the factors governing ionic conduction in composite electrolytes, develop new solid electrolytes based on LiRAPs effective for bonding between LLZ particles.

I describe the preparation of the LiRAPs-LLZs composite electrolytes that combine two different hardness solid electrolytes. Li_2OHBr (LHB) was prepared via a mechanochemical technique using a planetary ball mill ($LiOH + LiBr \rightarrow Li_2OHBr$). LHB -LLZs were mixed and moulded at 740 MPa and room temperature. The cross-sectional SEM image of the compact is shown in Fig. 1(a). The interface between LLZ and LHB particles are in good contact with each other. Fig 1(b) shows the variation in ionic conductivity with the LHB volume fraction in the green compact. The ionic conductivity of the green compact without LHB was 2.6 ×10^{-5} S/cm at 60 °C. The

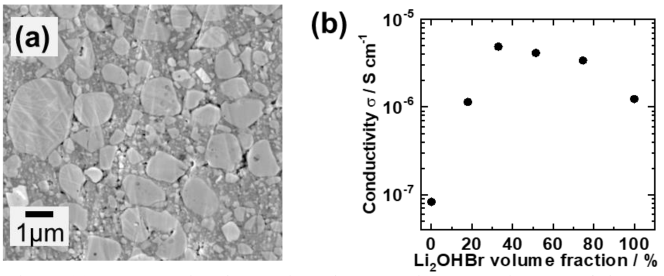

Fig. 1 (a) Cross-sectional scanning electron microscopy images of the green compacts of 50 vol%LHB-LLZ composites electrolytes. (b) Relationship between Li_2OHBr fraction of the green compacts and ion conductivity at 20 °C.

conductivity increased with the addition of LHB and reached the maximum conductivity (7.1×10^{-5} S cm^{-1}) at 30 vol% LHB. The wide contact area between LLZ and LHB particles at the interface led to an enhancement in ionic conductivity. The Nyquist plots were simulated and found to consist of three interfacial resistance components at LLZ/LLZ interface, LHB/LHB interface and LHB/LLZ interface. The LHB/LHB interface resistance component was identified as the main contributor to the electrolyte resistance at the 30 vol% LHB composition.

I describe the ion conductivity and mechanical properties of various mixed-chalcogen anions composed of $Li_{2+x}S_x(OH)_{1-x}Br_{1-y}F_y$ (x = 0 - 0.1, y = 0 - 0.1), synthesized by the ball-milling process. The observed XRD pattern was an antiperovskite structure in the cubic phase of space group $Pm\overline{3}m$. Fig. 2(a) shows the relationship between the amount of S^{2-} substitution and the ionic conductivity in the $Li_{2+x}S_x(OH)_{1-x}Br$ compact, which was pressed at room temperature. Fig. 2(b) shows the $P^{\frac{1}{2}}$–h lines of indentation hysteresis for the $Li_{2+x}S_x(OH)_{1-x}Br$ (x=0 and 0.05). The $Li_{2+x}S_x(OH)_{1-x}Br$ showed linear $P^{\frac{1}{2}}$–h lines under both composition. Meyer hardness (H_w) was calculated from the slope of the line. The H_w value decreased from 0.53 to 0.17 by the substitution with sulfur. This result indicates that the hardness of LiRAPs can be changed by partially substituting hydroxide with sulfide.

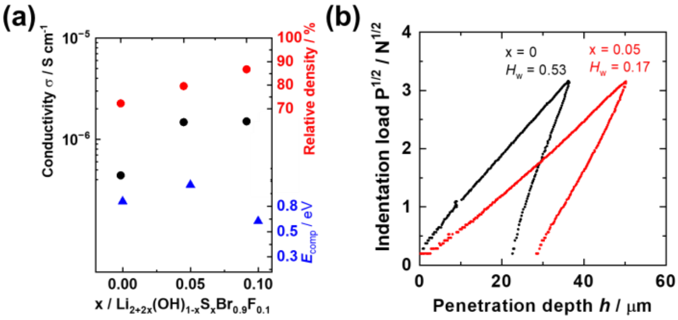

Fig. 2 (a) $P^{1/2}$–h curves of indentation hysteresis for $Li_{2-2x}S_x(OH)_{1-x}Br$. (b) The ion conductivity, relative densities and activation energy of $Li_{2+x}S_x(OH)_{1-x}Br_{1-y}F_y$.

The influence of anion substitution on ionic conductivity and electrochemical stability in LiRAPs was examined. Previous studies have indicated that the substitution of Br^- with F^- improves electrochemical stability, but simultaneously reduces ionic conductivity. The ionic conductivity of $Li_{2+x}S_x(OH)_{1-x}Br_{0.9}F_{0.1}$ increases with the increase in sulfides substitution. Sulfide and fluorine substituted LiRAPs were found to have improved electrochemical stability for cathode sweeps. These results show that the anionic substitutions are effective to enhanc ionic conductivity and electrochemical stability.

The sintering-free oxide-based all-solid-state cell was fabricated using a composite electrolyte and $LiFePO_4$ via uniaxial pressing at room temperature. The Li-In / 50vol%LHB-LLZ/$LiFePO_4$ cell exhibited reversible capacities of approximately 110 mAh g^{-1} at 60 °C. The cells in which LiRAPs were substituted with sulfide and fluoride demonstrated stable discharge capacities. These findings demonstrate the potential of non-sintering oxide-based LHB-LLZs composite electrolytes for use in all-solid-state lithium batteries.

All conclusions in this thesis are as follows; I developed the LiRAPs-LLZ composite electrolyte for sintering-free Oxide-base solid-state battery. The electrolyte becomes dense enough at low pressures without sintering. The composite electrolytes combining two solid electrolytes different hardness are effective approach for the realization of sinter-free processes. The combination of anion substitution was found to be an effective method for enhancing the electrochemical and mechanical properties of LiRAPs. In particular, my findings provide valuable information for the design of sinter-free processes for the practical implementation of oxide-based all-solid-state batteries, enabling them to meet the energy demands of next-generation applications.

論文審査結果の要旨

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本論文は、酸化物系固体電解質の機械的特性と固体電解質の粒子接触界面における固体界面形成の観点から無焼成プロセスによる酸化物系全固体リチウムイオン電池を開発した研究成果をまとめたものであり、以下の成果を得ている。

(1)$Li_7La_3Zr_2O_{12}$(LLZ)をベースに、Li_2OHBrを添加した複合電解質を作製し、その成型性とイオン伝導性について調べた。Li2OHBrの添加により、デンドライト成長の要因となる粒界や空隙を粉末の室温加圧のみで低減できることを見出した。特に、成型体内部におけるイオン伝導に対する抵抗要因を検討し、LLZ粒子間での界面抵抗が支配的でであることを見出した。Li金属を用いたLi/Li_2OHBr-LLZ/Li対称セルを構築し、Li金属に対する耐久性を評価した。60℃で対称セルを評価したところ、リチウム金属負極への展開に有望な機械的、電気化学的特性を有することを示した。
(2)Li_2OHBrをベースに、ハロゲン化物、カルコゲナイトを置換した場合の成型性とイオン伝導性について調べた。特に、S^{2-}による置換によって格子定数が増大することを見出し、10.8 GPaの低い弾性率を実現した。加えて、F^{-}による置換を組み合わせることで、さらに低い弾性率、高いイオン伝導度および活性化エネルギーの低減を実現した。
(3) 無焼成プロセスにより酸化物系全固体リチウム電池を作製した。In-Li合金を負極、$LiFePO_4$を正極活物質とした In-Li/Li_2OHBr-LLZ/$LiFePO_4$ 電池において、100 Wh/kg のエネルギー密度をもつ全固体リチウム電池の構築に成功した。

これらの結果は、全固体リチウム電池の開発に関する貴重なデータを提供し、高いエネルギー密度を有する全固体電池の発展に大きく貢献するところである。また、申請者が自立して研究活動を行うのに必要な能力と学識を有することを証したものである。学位論文審査委員会は、本論文の審査の結果から、博士（工学）の学位を授与することを適当と認める。