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研究課題名(和文) Design of electrode-electrolyte interface based on hybrid materials for all-solid-state lithium batteries using oxide solid electrolytes

研究課題名(英文) Design of electrode-electrolyte interface based on hybrid materials for all-solid-state lithium batteries using oxide solid electrolytes

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研究成果の概要(和文)：本プロジェクトでは、ポリエチレンオキサイド鎖を有する無機-有機ハイブリッド材料を合成し、ガーネット型固体電解質と高電位電極との界面材料として利用しました。この研究の主な結果を要約すると、次のようになります。(1) リチウムイオン伝導率が室温で 10^{-5} S cm⁻¹、活性化エネルギーが約0.5 eV、リチウムイオン輸送数が最大0.4、電気化学的ハイブリッド材料5Vまでのウィンドウが得られました。(2) 固体電解質とリチウム金属間の界面は、無機緩衝層を使用して改善されました。(3) 5.5 uAcm⁻²の電流密度を使用して室温で動作する全固体電池は、60 mAh g⁻¹の初期放電容量を達成しました。

研究成果の学術的意義や社会的意義

界面抵抗が高いため、全固体電池の実現は難しい。ここでは、無機成分と有機成分を含むハイブリッド材料を使用して、全固体電池用の新しいインターフェース材料を作成しました。ハイブリッド材料の無機部分は固体電解質と電極間の接着を改善し、有機部分はイオン経路を改善するために使用されます。持続可能な社会の発展には、今後の取り組みが期待されます。このプロジェクトは、申請者とプロジェクトに参加する学生の科学のおよび学問的な背景の成長に絶好の機会を提供しました。これらの結果の議論から優れたコラボレーションが生まれました。さらに、このプロジェクトを通じて、界面問題の新しい概念の導入が確立されました。

研究成果の概要(英文)：All-solid-state lithium secondary batteries based on oxide-type solid electrolytes are considered as a potential alternative for high energy density batteries, however, the high interfacial resistance between the electrodes and solid electrolyte has limited their real application. In this project, an inorganic-organic hybrid material with polyethylene oxide chains was synthesized and used as interfacial material between garnet-type solid electrolyte and high-potential electrode. The main results of this research are summarized: (1) Hybrid material with Li-ion conductivities of 10^{-5} S cm⁻¹ at RT, the activation energy of around 0.5 eV, lithium-ion transport number up to 0.4, and electrochemical windows up to 5V were obtained. (2) The interface between solid electrolyte and lithium metal was improved using inorganic buffer layers. (3) All-solid-state battery operated at room temperature using a current density of 5.5 uA cm⁻² achieved an initial discharge capacity of 60 mAh g⁻¹.

研究分野：Inorganic Chemistry

キーワード：hybrid materials interfacial resistance Li-metal batteries oxide solid electrolyte

様式 C - 19、F - 19 - 1、Z - 19 (共通)

1. 研究開始当初の背景

Rechargeable Li-ion batteries are powerful energy storage system with higher energy density and lower self-discharge rate than other types of rechargeable batteries. Li-ion batteries using organic liquid electrolytes and salts as source of lithium are successfully in various electronic devices that are part of our daily life due to the high value of the energy content. However, energy storage possible for commercial Li-ion batteries is not high enough for the long-term and large-scale needs of society, for example, extended-range hybrid or electric vehicles and smart grid technologies.

All-solid-state lithium batteries based on oxide-type solid electrolytes have attracted much attention as a possible candidate to achieve these challenge applications. Among oxide-type solid electrolytes, the garnet-type solid electrolytes (e.g. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, LLZ) have highest Li-ion conductivity at room temperature ($\sim 10^{-3}$ – 10^{-4} S/cm), high chemical stability against Li metal and wide potential windows with electrochemical decomposition voltage of 4-6 V vs. elemental Li anode. The realization of these all-solid-state lithium batteries is a challenging goal that has actively been investigated during the last years. The major drawback has been the difficulty in the formation of interfaces between electrodes and solid electrolyte because of insufficient percolation between particles resulting in a high interfacial resistance and in other words, poor lithium-ion and electronic conductivities. Table 1 summarizes some results obtained in this field focusing on solid-solid interfaces and including the first report in 2010.

Table I. All-solid-state lithium batteries based on LLZ (including doping) solid electrolytes using different strategies for low interfacial electrode/electrolyte resistance

Year	Cathode	Process / Temperature		Capacity (mAh g ⁻¹)	REF
2010	LiCoO ₂	Co-sintering	800 °C	0.015	1
2011	LiCoO ₂	PLD	-	125	2
2012	LiCoO ₂	PLD	-	130	3
2013	LiCoO ₂	Screen-printing	700 °C	85	4
2014	LiCoO ₂	Co-sintering	800 °C	78	5
2016	TiS ₄	PLD	-	500	6
2018	LiCoO ₂	Screen-printing	700 °C	94	7

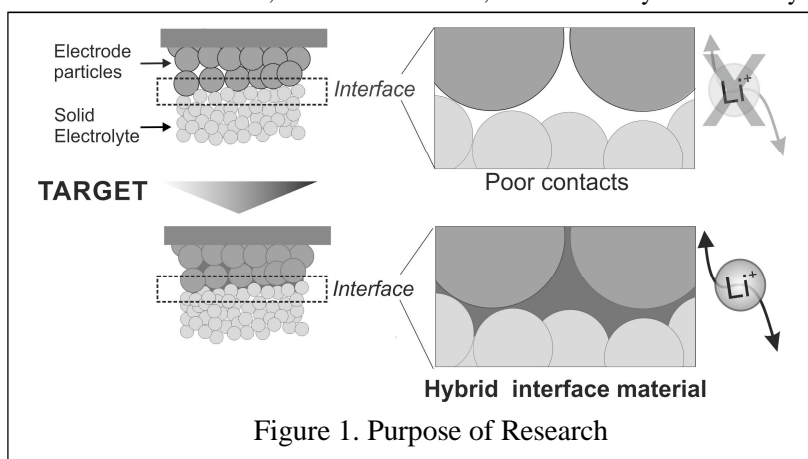
Kotubuki et al.¹ reported in 2010, the first all-solid-state battery using LiCoO₂ and lithium metal as cathode and anode, respectively. The interface between LiCoO₂ and LLZ was performed by the co-sintering process at 800 °C achieving 0.015 mAh g⁻¹ in the initial discharge capacity. The reason for low discharge capacity is associated with possible reactions at interface since the LiCoO₂ was deposited on the surface of the solid electrolyte by in-situ reaction using a precursor solution. Later, Ohta et al.²⁻⁵ have studied the deposition of LiCoO₂ by pulsed laser deposition (PLD)²⁻³, screen-printing⁴ (700 °C) and co-sintering (800 °C)⁵ processes achieving up to 130 mAh g⁻¹, 85 mAh g⁻¹ and 78 mAh g⁻¹ in the first discharge capacity, respectively. In the case of screen-printing and co-sintering processes, the use of sintering additive was necessary to improve the particle percolation, working as inorganic ‘binder’. The use of Li₃BO₃ has been used for this propose. The PDL process is rather effective to reduce the interfacial resistance since this process can produce a thin layer covering effectively the surface of the solid electrolyte including its defects (grain boundaries). This has also been used to apply other active materials films such as TiS₄⁶,

demonstrating the wide possibilities of LLZ in terms of the electrochemical window. From a scalable point of view, the PDL deposition has limitations and therefore, process such as screen-printing and co-sintering processes seems to be more attractive and realistic. In general terms, the screen-printing and co-sintering processes achieve lower discharge capacities than the PLD process since unfavorable reactions at the interface layer (e.g. formation of LaCoO_2) are promoted by the heating at high temperatures. Moreover, the heat treatment must be extended for several hours to reduce the presence of porosity and defects through the composite electrode, and in the end, the presence of voids is practically inevitable.

In this context, the present project aimed to new alternatives for the preparation of solid-solid interfaces at low temperatures. In the previous and parallel period of this proposal, other alternatives based on liquid-solid interfaces were also examined to prepare quasi-solid-state batteries based on LLZ solid electrolytes. Conventional organic liquid electrolytes are dropped at the surface of solid electrolyte or cathode/anode electrode layer to dramatically reduce the interfacial resistance. However, the use of these liquid-solid interfaces can suffer from the limitation of liquid electrolyte properties in terms of decomposition at high temperature (safety issues) and low current density operation.

2 . 研究の目的

The main objective of the research proposal was to design electrolyte/electrode interfaces with low resistance and obtained at low temperatures below 150 °C. Thus, the interface material was based on lithium ion conductive organic-inorganic hybrid solid electrolytes. The Figure 1 illustrate the general idea of this interface alternative. The poor contact between composite cathode and solid electrolyte is expected to be improved by the addition of hybrid material. The hybrid material contains an inorganic part (Si-O-Si network) to create an effective bonding with the electrode, while an organic part (polyethylene oxide, PEO, chains) was expected to enhance the ionic conduction paths. The liquid precursor of the hybrid electrolyte can easily wet the particles of electrode material and, after solidification, the formed hybrid electrolyte keeps an intimate contact with electrode material working as a traditional binder in Li-ion batteries, not only percolating particles but also, compensating the volume expansion during charge-discharge process and therefore, improving the cycle life of the battery.



3 . 研究の方法

The research was conducted in three different phases:

- (1) Preparation of hybrid material and evaluation of its electrochemical properties (60 %) including the chemical compatibility with cathode materials

(2) Study of LLZ/Li interface (15%)

(3) Preparation of LLZ/electrode using hybrid material and all-solid-state batteries. Formulation of different methods to apply composite electrode containing hybrid material and electrode (25%)

The hybrid material was prepared by liquid phase process and parameters of the synthesis were evaluated as a function of their electrochemical properties:

- Molar ratio of the inorganic, organic and hybrid precursors
- Effect of lithium source and concentration
- Heat treatment to consolidate hybrid material structure

The reactions of polymerization and polycondensation were studied to optimize the properties of the hybrid material to achieve high crosslinked structures. The electrochemical properties of the hybrid materials included ionic conductivity, electrochemical windows (up to 5V), and lithium ion transport numbers. Then, slurries containing hybrid material and active material were prepared to evaluate possible reactions during the further deposition in the all-solid-state battery.

The study of the LLZ/Li interface was necessary to understand the implications in the further construction of the all-solid-state battery. Organic interfacial buffer layers using ionic liquids and gel polymers were evaluated, and inorganic interfacial buffer layer were proposed for the first time.

Finally, the preparation of LLZ/electrode interface using hybrid material included the study and optimization of the weight ratio between active material and electrode. Electrochemical properties and battery test were evaluated. Then, different process to prepare composite electrode and apply it on surface of solid electrolyte was evaluated.

4 . 研究成果

The results are summarizing:

(1) Organic-inorganic hybrid precursor solutions using TEOS (tetraethyl orthosilicate), GPTMS (3-glycidoxypropyltrimethosysilane) and EGDE (ethylene glycol diglycidyl ether) with different lithium source and content were prepared. The hybrid material solution precursors are colourless, transparent and stable without the presence of precipitation for long time up to 3-4 months.

(2) Membrane prepared by casting and heat treatment with a temperature of maximum 120 °C showed high homogeneity/flexibility with thickness of ~800 μm. Incorporation of lithium salt does not produce appreciable changes in their aspect. High homogeneity was confirmed by high magnification observation.

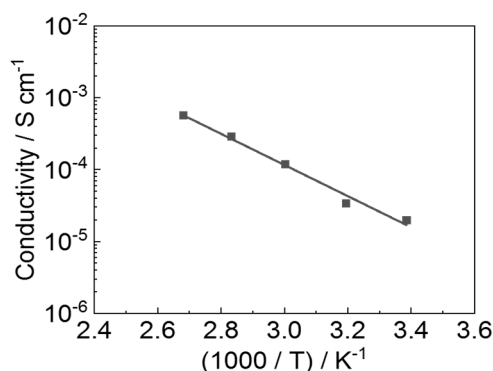


Fig.2 Temperature dependence of ionic conductivity of the hybrid material.

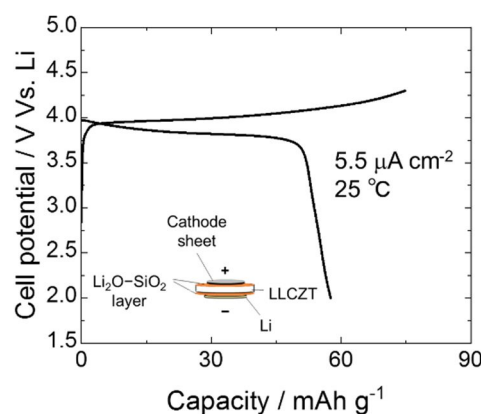


Fig.3 Charge-discharge curve of all-solid-state battery.

- (3) Li-ion conductivities of $10^{-5} - 10^{-6} \text{ S cm}^{-1}$ at room temperature, activation energy of around 0.5 eV (Figure 2), lithium ion transport number up to 0.4 and electrochemical windows up to 5V were obtained. Li^+ cation-polyether interactions are responsible of ionic conductivity in these materials, cations are solvated by ether oxygen's, moving by hopping into vacant donor sites. Improvement of lithium conductivity was observed by decreasing the amount of GPTMS precursor
- (4) High content of lithium lead to the drop of the conductivity (0.4 - 0.7 mol Li), since the formation of ion and anion interactions avoids the formation of complexes between ether oxygen's and lithium, which reduces the overall mobility and the number of effective charge carriers. Optimal lithium content of around 0.3 mol was determined.
- (5) Lithium silicate amorphous layer was used to reduce the interfacial resistance with lithium metal (N.C. Rosero-Navarro et al., *ACS Applied Energy Materials* 2020, 3, 6, 5533). The improved LLZ/Li using inorganic layer was performed without melt the lithium metal. The same buffer layer was also examined in the LLZ/cathode using lithium nickel cobalt manganese oxide (G. V. Alexander, N.C. Rosero-Navarro et al., *Journal of Materials Chemistry A*, 6, 2018, 21018). In this last case, the all-solid-state battery was operated at 100 °C.
- (6) The preparation of an all-solid-state battery using the hybrid material in the LLZ/electrode interface is schematically illustrated in the inset of Figure 3. The lithium silicate layer was used as an interface layer for anode lithium metal side and this was also used in the cathode side as a protective layer. Then, the composite electrode sheet was applied on the modified surface of solid electrolyte. The all-solid-state battery was operated at room temperature using a current density of $5.5 \mu\text{A cm}^{-2}$ achieving an initial discharge capacity of 60 mAh g^{-1} .

The perspective in this area should include the optimization of the method for the deposition of the hybrid composite electrode and the effect of solid electrolyte composition to achieve synergic properties with the hybrid material. The use of interfacial layers as LLZ/Li anode side seems to be promising since it does not require the lithium melting to produce low resistance interfaces.

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掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/C8TA07652A	査読の有無 有
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〔産業財産権〕

〔その他〕

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6. 研究組織

	氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
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