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「課程博士用」

学 位 論 文 の 要 旨

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学位論文題目	Development of composite solid-state electrolytes for all-solid-state lithium-ion batteries with electro-thermal modeling (全固体リチウムイオン電池用複合電解質の創製及びその熱解析).		

学位論文要旨

With the continuous development of energy storage battery technology and the transformation of production and daily life tools towards electrification, energy storage batteries have been widely applied in various fields, especially in the electric vehicle industry. Among various types of energy storage batteries, lithium-ion batteries stand out due to their excellent performance and have become the most widely used energy storage battery today. However, the widespread application of lithium-ion batteries has also exposed some of their shortcomings, with the biggest problem being safety issues. Due to the flammable organic liquid electrolyte used in lithium-ion batteries, they are very prone to catching fire and exploding under certain abusive conditions. Based on the series of issues encountered with liquid lithium-ion batteries, all-solid-state lithium ion batteries have become a good solution. Among various solid electrolytes, PEO-based composite solid-state electrolytes have good interface properties and low interfacial impedance, and require no liquid solvents during preparation, making PEO-based composite solid-state electrolytes one of the most promising electrolytes for research. However, as all-solid-state lithium ion battery technology has matured in recent years, some studies have also shown that all-solid-state lithium ion batteries carry the risk of thermal runaway. Therefore, it is necessary to establish a thermal model for all-solid-state batteries in advance to provide guidance for their design. Against this background, the following research work has been carried out:

Firstly, a low-cost foldable nano-Li_2MnO_3 integrated Poly(ethylene oxide) (PEO) based composite polymer solid electrolyte (CPSE) is prepared by simply solid-phase method. Density functional theory calculations indicate that the LMO could provide faster ion transfer channels for the migration of lithium ions between PEO chains and segments. As such, the obtained CPSE has a high ionic conductivity of 5.1×10^{-4} S cm^{-1} at 60°C with a high lithium ions transference number of 0.5. While, the CPSE remains stable even at high temperature with no thermal runaway occurring, which should be benefit for the improvement of safety performance of the batteries. Secondly, a low-cost flexible Li_2SnO_3(LSO)-coupled PEO-based composite single-ion conducting polymer solid-state electrolyte (CSIPE) was prepared by a simple solvent-free solid-phase method. The obtained LSO-coupled CSIPE exhibited a high ionic conductivity of

5.59×10^{-4} S cm^{-1} at 60°C with a high lithium ion transference number of 0.54 and an electrochemical stability window as high as 5.28 V. In addition, the results based on Vogel-Tammann-Fulcher (VTF) model and differential scanning calorimetry (DSC) measurements indicated that the presence of LSO reduced the activation energy for lithium ion migration and the crystallinity of the polymer matrix to provide channels and flexible polymer chains for the transportation of lithium ions. Moreover, the CSIPE also demonstrated an excellent rate performance and outstanding adaptation to cathodes. Furthermore, the obtained LSO-coupled CSIPE remained stable even at a temperature as high as 322°C without thermal runaway, and worked under different current densities for 450 hours without short-circuiting, indicating good interfacial stability to ensure the safety of the batteries. Finally, we proposed a novel and universal thermal model mechanism for lithium ion batteries. We validated the model by combining it with commercially available 18650 batteries and testing the electrochemical parameters of PLL composite solid-state electrolyte. We developed a computational model for all-solid-state lithium ion batteries based on PLL composite solid-state electrolyte, and the simulation results showed that the maximum temperature of all-solid-state lithium ion batteries based on PLL composite solid-state electrolyte and commercial standards are significantly lower than the thermal runaway temperature of solid-state electrolyte. However, as the temperature increases, the heat generation of the battery will gradually increase, which will reduce the efficiency of the battery. At the same time, if the temperature of the battery varies greatly under different operating conditions, it will cause great difficulties in the design of other ancillary components and even lead to certain safety issues. Therefore, from the perspective of performance and practical application, composite solid-state electrolytes should be improved towards the direction of improving ion conductivity at low temperatures in order to have better commercial prospects.

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