Synthesis of Amorphous Oxide Electrolyte Nanoparticles for All-Solid-State Battery by Induction Thermal Plasma

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論 文 名　：Synthesis of Amorphous Oxide Electrolyte Nanoparticles for All-Solid-State Battery by Induction Thermal Plasma　（誘導結合型熱プラズマによる全固体電池用アモルファス酸化物電解質ナノ粒子の合成）

区　　分　：甲

論　文　内　容　の　要　旨

All-solid-state battery (ASSB) is considered a promising candidate for next generation battery due to the non-flammable, high energy density, and no leakage. However, the solid state of electrolyte results in low ion conductivity, poor connectivity, and strong interfacial resistance between electrode and electrolyte. Amorphous oxide solid electrolyte is introduced to improve these problems. The amorphous structure ensures the easy transition of Li ions because of the sufficient structure defects. The sable electrochemical property of oxide avoids harmful gas generation during cycling. High Li content in compounds promise high ion conductivity due to more ion carriers. Moreover, decreasing solid electrolyte particles to nanoscale also benefits ion conductivity owing to the larger connect area between electrode and electrolyte. Thus, amorphous oxide nanoparticles are regarded as the promising candidate for solid electrolytes. Amorphous Li_3BO_3, Li_4GeO_4, and Li_5AlO_4 nanoparticles are selected as target material because of the high Li content, simultaneously, the B, Ge, and Al can act as good glass former. Induction thermal plasma characterized by electroless discharge, high temperature (> 10^4 K), and rapid quenching rate (10^3-10^6 K/s) is appropriate for synthesis of amorphous nanoparticles with high purity. In this dissertation, amorphous Li_3BO_3, Li_4GeO_4, and Li_5AlO_4 nanoparticles are synthesized by induction thermal plasma, the formation mechanism and formation ability of amorphous nanoparticles with high Li content during plasma process are also investigated.

In chapter 1, the method of induction thermal plasma and ASSB are generally reviewed. Meanwhile, the objective of this dissertation is put forward.

In chapter 2, synthesis of amorphous Li_3BO_3 nanoparticles by induction thermal plasma is conducted systematically with the investigation of the formation mechanism. Agglomerates in products are observed due to the lower temperature of nanoparticle growth region. Lithium borate nanoparticles are synthesized after Li_2O nucleation, Li_2O and $LiBO_2$ co-condensation, and coagulation. The Li_3BO_3 is mainly synthesized at the early stage of condensation after a series of borate unit transformation. The by-product Li_2CO_3 is formed during collection by uncondensed Li_2O reacting with H_2O, and CO_2 in atmosphere. Enhanced quenching rate leads to higher amorphous Li_3BO_3 degree because of the impediment of particle order growth. While, the enhanced quenching rate also results in insufficient borate unit transformation, which increases the percentage of by-products.

In chapter 3, amorphous Li_4GeO_4 nanoparticles are successfully synthesized by induction thermal plasma. Formation mechanism is investigated based on thermodynamic analysis, and the nucleation phase is identified as Li_2O. The Li_4GeO_4 and Li_2GeO_3 nanoparticles are mainly synthesized at early and following stages of co-condensation respectively because of the discrepancy in Li_2O and GeO saturation ratio. The enlarged intratetrahedron O-Ge-O angle distribution is achieved in high Ge molar content and quenching rate, which increases disorder in short range. The high quenching rate also allows the broader intertetrahedron Ge-O-Ge angle distribution to be preserved, acquiring the more chaotic state in intermediate range order. Enhanced amorphous Li_4GeO_4 degree and fraction of high temperature phase γ-Li_4GeO_4 are obtained in high Ge content and quenching rate conditions. However, the excessive quenching rate and Ge content result in more by-product Li_2GeO_3 synthesis.

In chapter 4, thermal plasma synthesis and formation mechanism of amorphous Li_5AlO_4 nanoparticles are studied. The synthesis and nucleation of Al_2O_3 occur simultaneously. The Li_5AlO_4 is mainly synthesized after aluminate unit transformation from [AlO_6] octahedron to [AlO_4] tetrahedron with Li and LiO vapor condensation. The increased Li/Al molar ratio and quenching rate contribute to amorphous Li_5AlO_4 nanoparticles formation due to more LiO participating in reactions and the promoted aluminate unit transformation. However, the enhanced quenching rate also causes more early solidification of nanoparticles. The transformation time is shortened, and more [AlO_6] octahedrons are preserved in products.

In chapter 5, the formation ability of amorphous nanoparticles with high Li content synthesized by induction thermal plasma is investigated by comparing experiment results of Li-B-O, Li-Ge-O and Li-Al-O systems. The formation ability is discussed from amorphous structure and chemical composition, respectively. The system with a network built by strong bonds prefers to achieve amorphous structure after plasma process because the topological disorder network is more easily preserved. The shorter time lag of co-condensation benefits the synthesis of products with uniform chemical composition. Meanwhile, the sample structure unit transformation also contributes to reducing the by-product synthesis.

In chapter 6, the summarized conclusion and future works are presented.

In summary, the results from this study provide an insightful understanding of amorphous nanoparticles with high Li content synthesized induction thermal plasma, which contributes to the development of ASSB with high performance.