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Synthesis of Amorphous Oxide Electrolyte
Nanoparticles for All-Solid-State Battery by
Induction Thermal Plasma
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令和五年度 博士論文

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1.1 General Introduction of Plasma

Solid transform into liquid after heating and further become gas with continuous heating. The gas would be ionized upon further heating and finally form into plasma. Plasma consists of ions, electrons, atoms, and molecules. Plasma is sometimes called the "fourth state of matter" [1].

Plasma occurs commonly in nature. The most known matter in the universe is the ionized state, namely, many known matters exist as plasma in the universe [2]. The solar corona, solar wind, nebula, polar, and earth's ionosphere are considered plasma. **Figure 1.1** shows the domains of plasma as the function of temperature and electron density. Irving Langmuir introduced the term plasma for the first time. He thought the ionized gas near electrodes contains ions and electrons in about equal numbers except for the sheaths, which leads to the space charge being very small. Furthermore, he suggested using plasma to describe the balanced charges of ions and electrons [3]. Not any ionized gas can be called plasma from the suggestion of Irving Langmuir, because quasineutral is a significant index. Therefore, the definition of plasma shows the following: A plasma is a quasineutral gas of charged and neutral particles exhibiting collective behavior [1]. Benjamin Franklin conducted a significant experiment to verify the plasma formed in nature with lighting. This interesting experiment also illustrates people's strong interest in plasma.

Plasma also can be generated in the laboratory easily with various methods current, called manmade plasma. Plasma can be produced by direct current (DC), alternating current (AC), or radio frequency (RF) sources at high pressure (> 10 kPa). The plasma temperature can achieve a relatively high level around $2 \times 10^3 \sim 2 \times 10^4$ K with electron densities ranging from 10^{21} to 10^{26} cm⁻ ³. Above plasmas are characterized by high energy density and equality between heavy particles (*T_h*) and electrons (*T_e*) temperature. These plasmas are called thermal plasma or equilibrium

plasma [4,5].

Another type of plasma is cold plasma or non-equilibrium plasma because this plasma is not thermodynamic equilibrium and $T_e > T_h$. The temperature range of heavy particles is from 298 K to 373 K, while the electrons have much higher temperature from 5000 K to 10^5 K [6]. Meanwhile, non-equilibrium plasma systems are in most cases operated at low pressures (< 10 kPa) and have lower electron density from 10^9 to 10^{10} cm⁻³. Most electrons have kinetic energy below 20 eV. Glow discharge and low pressure RF discharge are common measures to obtain cold plasma [7,8]. **Figure 1.2** presents the typical ranges of electron temperature rang with electron density for nonequilibrium and equilibrium plasma.

There is a wide application of plasma, such as coating, waste treatment, metallurgy, and material synthesis, in the industry owing to their unique superiorities. However, the hydrodynamics, complex electric and magnetic fields lead to plasma becoming a complicated subject. Therefore, further and continuous study of plasma is necessary both for theoretical research and commercial applications.

1.2 Thermal Plasma

1.2.1 Complete Thermal Equilibrium

There are temperature dependencies that exist in an ideal thermal plasma, such as excited states of atoms, ionization degree, electron density and internal heat exchange by radiation. Complete thermodynamic equilibrium (CTE) is a significant index for ideal thermal plasma [9]. The velocity and energy distribution of particles in thermal plasma conform to Maxwell-Boltzmann distribution:

$$f_j = n_j \left(\frac{m_j}{2\pi KT}\right)^{3/2} \exp\left(-\frac{m_j v^2}{2KT}\right)$$
(1-1)

where n_j and m_j are number density and mass of particle of j, respectively. Boltzmann constant is presented as K. T and v represent temperature and velocity, respectively. Simultaneously, the number density of heavy particles in the excited state also satisfies the Boltzmann distribution. The excitation temperature is same for all excited states and equal to the temperature in Maxwell distribution. There is a relationship between number density of particles in different states:

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} \exp\left(-\frac{\Delta E}{KT_{ex}}\right)$$
(1-2)

here, n_i and n_j represent the number density of particles in an upper *i* and lower state *j*. g_i and g_j are the statistical weights, respectively. Energy difference between *i* and *j* state is presented as ΔE , excitation temperature is presented as T_{ex} .

Number density of particles in thermal plasma should satisfies law of mass action during chemical reactions process, such as dissociative-recombination reactions and ionization-recombination reactions. The law can be described as Saha Equation in gas ionization reactions:

$$\frac{n_{r+1}n_e}{n_r} = \frac{2z_{r+1}}{z_r} \frac{(2\pi m_e K T_{reac})^{3/2}}{h^3} \exp\left(-\frac{E_{r,i}}{K T_{reac}}\right)$$
(1-3)

where n_r and n_{r+1} are the number density of particles in the *r*-th and (r+1)-th state of ionization, z_r and z_{r+1} are the partition function of two particles; $E_{r,i}$ is the ionization energy and T_{reac} is the ionization temperature; m_e and h are electron mass and Planck constant, respectively. Ionization decrease should be considered in high temperature and high number density. Similar equation for atom dissociation reactions also can be obtained according to above. In thermal equilibrium, T_{reac} is the temperature of dissociation and has the same value for all possible reactions involved. Simultaneously, T_{reac} equals T_j in Maxwell distribution and T_{ex} in Boltzmann distribution.

The electromagnetic radiation for thermal plasma is obeyed the Planck law of black body radiation, namely the relationship between radiation intensity B_v and frequency f is described as the following equation:

$$B_{\nu} = \frac{2h\nu^3}{c^2} \frac{1}{\exp\left(\frac{h\nu}{KT_{rad}}\right)} -1$$
(1-4)

where *c* is the speed of light and T_{rad} is the black body radiation temperature. There is a relationship among the temperature in complete thermal equilibrium plasma which is presented as following:

$$T_h = T_e = T_{ex} = T_{reac} = T_{rad} \tag{1-5}$$

Actual thermal plasma is difficult to satisfy above requirements, especially for the electromagnetic radiation. The measured radiation intensity of thermal plasma is much lower than black body radiation intensity because plasma cannot be treated as black body with the broad wavelength region. Plasma even is treated as optically thin, that is the plasma cannot absorb radiation. Hence, the T_{rad} would lower than other temperature in plasma. Besides, thermal conduction, thermal convention and diffusion of vapor components also lead to the deviation of thermal equilibrium in plasma.

1.2.2 Local Thermal Equilibrium

Laboratory and industrial plasma are difficult to achieve the complete thermal equilibrium, local thermal equilibrium (LET) is introduced to describe the thermal plasma. Plasma can be treated as optically thin in LET which is different from CTE, that is, plasma radiation intensity does not equal black body radiation intensity at the same temperature. The LTE can be achieved by energy state transition and chemical reactions in thermal plasma dominated by collision. A detailed equilibrium exists between the collision process and its reverse process. The temperature and concentration gradient also should be relatively low in order to allow the LET. The temperature in thermal plasma should follow the relationship:

$$T_e = T_h = T_{ex} = T_{reac} \tag{1-6}$$

The Maxwell distribution, Boltzmann distribution and Saha equation are still available. Hence, the process in thermal plasma except radiation is still temperature depended. The plasma should be kept at relatively higher level of number density (> 10^{23} m⁻³) and vapor pressure (≥1 atm), aiming to achieve the high collision frequency between electron and heavy particles.

1.2.3 Thermal Plasma Generation

Arc discharge and high frequency inductive coupling discharge are the main methods to generate thermal plasma with temperature over 10⁴ K in laboratory. Microwave discharge and laser heating are other common methods [4].

I. Direct Current Arc Plasma

Arc discharge is considered a convenient method to generate thermal plasma. The arc consists of arc column, cathode region, and anode region. The arc column occupies a temperature as high as 10^4 K and is electrically neutral, showing a thermal plasma state [10]. The arc for thermal plasma generation has a high current density which can reach $10^7 \sim 10^8$ A/m². Arc plasma is usually generated at atmosphere pressure, the energy that electron obtains from electric field is much lower than gas ionization energy. Thus, the gas ionization mechanism for plasma is thermal ionization rather than field ionization.

Cathode and anode region take account of small percentage of the arc volume and are not electrically neutral. There are two types of electrodes for direct current (DC) arc plasma generator. The mental, such as tungsten, with high melting point is used as cathode called thermionic cathode. Electrons thermionically emit from the cathode and enter anode which is usually made by graphite passing through arc column. The arc plasma generator with thousands of watts or tens of kilowatts always uses thermionic cathode [11]. Another type is called non-thermionic cathode, the cathode

and anode are made of the same material which the mental has high thermal conductivity and low melting point. Temperature-aided emission is considered the electron emission theory. The high-power plasma generator always selects non-thermionic cathode [12].

The DC arc plasma generators can work as following method. Figure 1.3(a) shows the first form which the cathode and anode are inside of the plasma generator, the plasma flows out of the generator after gas is heated by the inside arc. This type of arc is called non-transferred arc and is usually utilized in plasma spray and arc gas heaters [13,14]. Figure 1.3(b) shows another generator which the inside anode only assists with arc generation. The workpiece would be worked as the main anode during the working. Arc welding, plasma cutting and non-ferrous metal melt are the main application of this arc which is named transferred arc.

Free-burning arc is a simple gaseous discharge contrasted to above two types because there is no limitation in it. The interaction of arc current and its magnetic field lead to the induced plasma jet in high-intensity arc region of variable cross section. The gas surrounding cathode is drawn by the electromagnetic filed and ejects to anode region. A stagnation layer would be formed in front of anode, then the free-burning arc with bell is formed [15]. The free-burning arc only can be stable in the short distance between cathode and anode. **Figure 1.3 (c)** shows the diagram of freeburning arc. Welding, arc furnaces, switchgear, and arc heaters are important industrial applications for free-burning arc [16].

II. Alternating Current Arc Plasma

The power supply for arc generation can use alternating current (AC) besides DC. The arc power source affects the polarity of the electrical current that runs through the electrode. The AC arc is more efficient and reliable in contrast to DC arc. Because it does not need to utilize AC-DC

current rectification which takes accounts for around 30% of the overall capital and operation cost of most plasma installations [17].

Multiphase AC arc is the most major part of AC arc, its schematic diagram is presented in **Fig. 1.3(d)**. There are several arcs coexist in a large discharge chamber volume, which leads to a large arc volume. Meanwhile, the multiphase alternating current also allows the continuous plasma even during the zero-current crossing. Above advantages promise the multiphase AC arc is treated as an appropriate method in waste treatment, pyrolysis, gasification, and nanoparticle synthesis [18–21].

III. Radio Frequency Induction Thermal Plasma

The plasma generated by arc is polluted by metal due to the erosion and melting of electrodes, which negatively influences plasma application to some extent [22–25]. Radio frequency (RF) thermal plasma can offer a pure environment owing to coupling discharge [26,27]. The electrons move in an opposite direction in opposite periods of alternating electric field, the length that electron moves in a half period can be obtained. The electron in discharge region would collide with other particles instead of arriving at electrodes, when the distance between two electrodes over this length. The discharge can be maintained in a situation that provides additional electric field, simultaneously, electrode can locate outside of discharge tube [1].

Capacitive coupling is one of the methods to generate RF plasma, the anode and cathode exist out of discharge tube. The advantage of capacitive coupling is maintaining discharge under relative lower power. While the plasma generated by capacitive coupling discharge is non-thermal plasma [28,29].

Thermal plasma is always generated by inductive coupling discharge due to its high efficiency. The plasma generated by this method is called RF induction thermal plasma. Reed reported that

thermal plasma was generated with atmosphere pressure and flow gas first time in 1961 [27]. The RF induction thermal plasma has already been widely used in various fields, such as spraying, nanoparticle synthesis and spectrum analysis [30–33]. The torch consists of a quartz tube and copper coil, the diagram is shown in **Fig. 1.3(e)**. The power supply offers high frequency current passing through the coil, which leads to magnetic field generation. This magnetic field would be couple with the plasma in the quartz tube. The sheath gas injects into plasma torch would be conductive after ignition. The excitation current which passes through coils would produce an alternating magnetic field, further leading to the alternating electric field. The current would be generated in the conductive gas in the quartz tube and produce Joule heat. The thermal plasma can be maintained with the appropriate discharge conditions, meanwhile, the continuously injecting cold gas is heated to form thermal plasma [27]. Since RF induction thermal plasma is electrodeless discharge and has a flexible atmosphere (Ar, He, H₂, O₂ and N₂), it is treated as an ideal method to produce material with high purity and heating sample for spectrum analysis [34,35].

Skin effect is a basic process of screening out electromagnetic fields by plasma. Skin depth is a significant index for induction thermal plasma and expressed as:

$$\delta = (\pi \xi_0 \sigma f)^{-1/2} \tag{1-7}$$

where δ is skin depth, ξ_0 is magnetic permeability. The conductivity σ is 2700 S/m around 10⁴ K for Ar plasma. The δ is around 1.53 mm and 5.6 mm for *f* is 4 MHz and 3MHz, respectively. Skin depth decreases with frequency increase based on the above results, simultaneously, plasma Joule heat would concentrate on the narrow region when frequency increase. Coupling effect would be optimal when the discharge radius is 1.5 times skin depth according to experience [4,36]. The ratio of discharge radius to coil radius is another index for coupling efficiency, the enhanced efficiency can be obtained at higher value [37].

The minimum power to maintain discharge is affected by frequency, generator diameter, and gas pressure. Low frequency and large diameter result in high minimum power, high vapor pressure has the same effect. Argon is an excellent candidate to ignite induction plasma because of its lowest minimum power value. Mixture plasma can be obtained by injecting other gas into Ar plasma after ignition.

IV. Microwave Plasma

Microwave discharge also plays a critical role in thermal plasma generation. There is a wide range in pressure and frequency of microwave plasma. The microwave plasma can be sustained with frequency from 1 MHz to 10 GHz, the discharge pressure ranges from 10⁻³ Pa to hundreds of kPa [38]. Electrons are also responsible for energy absorption from electric field same as arc and coupling discharge. The low pressure microwave discharge (< 10 kPa) would generate non-thermal plasma. Because the kinetic equilibrium deviation is caused by poor collision between electrons and heavy particles [39]. Thermal plasma can be obtained at high pressure conditions (> 10 kPa). Electromagnetic surface wave and traveling wave discharge are two selections for microwave plasma devices, the latter is stable, reproducible and quiescent contrasted to the former [40,41].

1.2.4 Thermal Plasma Application

Advanced technology always drives advanced productivity. Thermal plasma technology as an efficient and progressive method has a wide application in industry and daily life ascribing to its unique superiorities. The application mainly focuses on two areas: material processing and treatment of waste. Several mature sciences with considerable economic activity have already been established for material processing. The object of waste treatment is recovering the products

with higher added value and decomposing the toxic wastes in the waste treatment region [42]. Specific details will be described in the following.

I. Metal Melting and Remelting

Thermal plasma is used as an effective source for heating process, the metal can be melted under inert gas atmosphere (He or Ar) with a wide pressure range. The maximum temperature can be over 15000 K which allows metal and alloy to melt totally. Meanwhile, the evaporation of metal and alloy can be inhibited under plasma process, and enhance the possibility of complex alloy material synthesis. A wide range of plasma process is possible and mature technology has already been applied to industry [43,44].

Metallurgical industry is one of the important applications of plasma melting. High concentration and thermal efficiency, excellent heat and mass transfer, and adequate residence time allow transferred arc device to be utilized in metallurgy widely. Synthesis of high purity synthetic silica, ultrafine high purity ceramic powders and production of high purity titania slag from ilmenite have already been achieved [45–47].

II. Plasma Cutting and Welding

Plasma cutting is a melting process that cuts through electrically conductive materials by accelerated jet of hot plasma. Arc would be generated between cathode and the workpiece which is used as the anode. Recombination of particles takes place when plasma hits the workpiece and emits heat simultaneously [48]. The workpiece would be melted by emitted heat and gas flow ejects it from the cut [49]. Argon, nitrogen, or mixture of Ar and H₂ are the common plasma generation gas for cutting. Inert gas prefers to cut workpieces made of reactive alloys. In addition, the inert gas can be replaced by air, the cathode material also should be replaced by hafnium or

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zirconium [50]. Compressed air is more competitive to cut carbon-manganese and stainless steel up to 20 mm contrasted to oxygen-fuel cutting [51]. The subject of plasma cutting is various, such as aluminum and its alloy, nickel and its alloy, and titanium. These materials cannot be cut by oxygen-fuel cutting due to the low satisfactorily [52,53]. Robert M. Gage developed this cutting method in 1957 which promoted material processing to great extents.

The arc is formed between a pointed tungsten cathode and the workpiece which is used as anode during plasma welding process. The plasma arc is separated from the shielding gas because the electrode is placed within torch body. Coalescence is produced by the heat from the arc. Inert gas is utilized during this welding for plasma generation or shielding the arc plasma [48,54]. Robert M. Gage developed this method in 1953 and allowed the precision operation on both thin and thick metals.

III. Plasma Spraying Coating

Plasma spraying technology is a coating process in which material melted by thermal plasma is sprayed on the surface of workpiece. This technology allows thin coating (from several to 20 mm) formation and high rate deposition on a large area contrasted to conventional fabrication methods, such as electroplating, physical and chemical vapor deposition. There is a wide range of coating material options, especially for the high melting point material, owing to the high temperature of thermal plasma [55]. Metal, alloys ceramic, plastic, and composition are all available for coating material [56]. The material particles are fed into the torch and heated to melting state, then accelerated towards to substrate. The whole spraying process is the accumulation of numerous sprayed particles. The surface of substrate is in low temperature state, which can achieve flammable substrate coating [57,58].

This technology appeared in the 1960s and was developed in the 1980s due to plasma torch improvement. Simultaneously, plasma spraying was devoted to implementation of robust sensors which work in hard environments. Now plasma spraying is mainly applied to processing highadded value coatings [59].

IV. Plasma Spheroidization and Densification

Spherical particles have lots of superiorities in industry applications. The sphere state improves powder flowability, increases powder packing density, eliminates particle internal cavities and fractures, changes surface morphology, and enhances powder purity [60]. Hence, spherical particles are ideal options for various industry fields, such as powder metallurgy and thermal spraying. The RF induction thermal plasma is considered an efficient method for spheroidization because the high temperature and long residence time promise particles evaporate completely [61]. Particles coalesce faster than coagulate and spherical particles are formed at high temperature during particle growth [62]. The high temperature ensures that spheroidization and powder densification occur simultaneously. Agglomerates are injected into thermal plasma and form densified powder after sintering. There is a wide range of subjects from metals (eg. W, Mo) to high technology ceramics. Plasma densification costs less time, restrains grain growth and tailor heat transfer compared to conventional method, which provides more possibilities to obtain sintered particles with desirable structure [5].

V. Waste Treatment

Waste treatment is another critical application in thermal plasma besides material processing. Since conventional methods for waste treatment, such as landfills and ocean dumpsites, become less and less available, searching for new methods is urgent. Incineration has been utilized

increasingly due to most waste is combustible [63]. However, this method results in plenty of fossil fuel consumption and hazardous gas and slag production, which means no complete treatment of waste [64].

Thermal plasma provides a controlled heat source to melt feedstock and to maintain a high temperature molten bath. The high temperature allows chemical bond destruction and substance vaporization, which decreases slag production. Moreover, thermal plasma treatment also achieves energy production and recuperation of by-products during processing [65]. Namely, waste can be regarded as a green energy source. The synthetic gas which is consisted of H₂ and CO can be obtained from municipal solid waste during the plasma treatment [66,67]. This synthetic gas is more easily to achieve completed combustion compared to methane, simultaneously, also can be used to generate electricity [68]. Waste gas treatment of acetylene production by thermal plasma has already been a commercial application [69].

VI. Nanoparticle Synthesis

The research and development at the atomic, molecular, or macromolecular scales are defined as nanotechnology. Nanoparticles that have a diameter of less than 100nm are the most important component for nanotechnology [70]. The properties of material consisting of nanoparticles are different with their bulk and molecular material owing to their tiny size, in particular for electronic, magnetic, optical, biomedical, catalytic, and energy [71–75]. Therefore, nanoparticle synthesis is a field that attracts people's attention. Biological synthesis, co-precipitation, thermal decomposition and reduction, micelle synthesis, hydrothermal synthesis, and laser pyrolysis technique are common methods to obtain nanoparticles [76–78].

Thermal plasma is used to synthesize nanoparticles due to the high chemical reactivity, high enthalpy, and steep temperature gradient [79]. Furthermore, thermal plasma also allows

spheroidization and densification simultaneously. Above superiorities indicate thermal plasma is a promising method to obtain nanoparticles with better morphology and narrow size distribution. **Figure 1.4** is the diagram of nanoparticles synthesized by thermal plasma. Various nanoparticles have already been synthesized by thermal plasma and more details will be described in the following.

1.3 Synthesis of Nanoparticle by Thermal Plasma

Thermal plasma is applied widely as an efficient and advanced fabrication method of nanoparticles. Different types of nanoparticles are synthesized by different thermal plasma according to their respective properties to ensure the high quality of products.

1.3.1 Method for Synthesis of Nanoparticles

I. Transferred DC Arc Plasma

Transferred DC arc plasma considered an efficient heat source is widely utilized in metal nanoparticles with a diameter of less than 50 nm synthesis [80]. The chemical composition of electrode is same as the target material for this device, the arc plasma is generated by evaporating electrode directly. In addition, most of target material can be used as electrode for transferred DC arc plasma torch. These situations lead to the application of transferred DC arc plasma spreading rapidly. A series of research related to generation rate of nanoparticles and physical properties of electrode was conducted [81]. Sixteen metals are selected as electrodes and the experiment results indicate that Mn, Ag, and Al are easy to obtain nanoparticles, while Mo, Ta, and W are difficult to form into nanoparticles. According to experiment results and thermodynamic calculations, the research concludes that the driving force of nanoparticle generation relates to vaporization heat and melting point of metal. Meanwhile, adding diatomic gas, such as N₂ and H₂, benefits to metal

vapor generation. Further research also investigates the morphology of electrode, revealing spherical shape has a positive on evaporation [82].

II. Non-transferred DC Arc Plasma

The consumption of electrode during nanoparticle synthesis process in transferred arc plasma results in the discontinuous fabrication. Non-transferred DC arc plasma torch is introduced to solve this problem. Different from transferred arc the electrode in this setup is only for generating and maintaining thermal plasma. The raw material is injected into thermal plasma flame during plasma process [83]. The injection port is usually located in the torch exit, which is similar to plasma spraying device [84]. However, this results in the evaporation of raw material incomplete, further influencing the quality of fabricated nanoparticles negatively. Some researches show that the raw material particles are far from a full evaporation state in non-transferred arc torch [85].

III. Multiphase AC Arc Plasma

The DC power supplies are used to generate DC arc plasma, this situation requires converting AC power to DC power. Conversion from AC to DC results in higher energy cost [86]. Synthesis of nanoparticles by AC arc plasma attracts lots of interest in order to achieve the goal of energy saving. The AC arc plasma can be generated directly by the AC power. Single-phase and three-phase are two usually utilized power supplies. However, the intermittent discharge caused by the polarity transition results in a momentary zero current [20]. The synthesis process is limited by the zero current, further affecting the nanoparticle quality. Multiphase AC arc plasma is introduced aiming to improve this problem. The advantages of multiphase AC arc plasma, such as high energy efficiency, large plasma volume, low gas velocity, and low cost, allow it

appropriate for synthesize large amounts of nanoparticles [87]. While the erosion of electrodes would pollute the synthesized nanoparticles and decrease the purity of products.

IV. Induction Thermal Plasma

Ratio frequency induction thermal plasma attracts lots of attention because it can prevent incomplete heating of raw material and also can eliminate electrode pollution. Different from arc discharge, RF plasma discharge is generated by coupling instead of electrode discharge. In addition, the larger plasma flow and continuous discharge also contribute to unit and spherical nanoparticle generation [80]. Electrodeless discharge offers an ideal environment for high purity nanoparticle synthesis. The unique structure of RF plasma torch allows axial injection of raw material alone the centerline, which leads to more effective heating. The RF induction thermal plasma is popularized rapidly in nanoparticle fabrication according to above description, and various products with high performance have already been obtained [88,89].

1.3.2 Nanoparticles synthesis by thermal plasma

I. Metal

Properties change would occur when metal particle diameter decreases to less than 50 nm because of the size effect [80]. Since the electron confinement of metal particles increases with diameter decrease, new properties are observed with the metal to insulator transition [90].

Iron nanoparticles offer very potent magnetic and catalytic properties, while their systematic research is difficult to conduct until the advanced fabrication method occurs [91]. Nanoscale Fe particles have already been synthesized by RF thermal plasma [92]. The raw material with diameter ranging from 25 μ m to 37 μ m was injected into thermal plasma because full evaporation can be achieved by Fe particles with this diameter range [93]. The size of fabricated nanoparticles

is $6 \sim 12$ nm with different feed rates and residence time. Increased feed rate and residence time lead to larger particle synthesis. Prepared nanoparticle morphology was also detected by electron microscopy. Three typical types of morphology are observed, they are spherical, rhombic dodecahedral bounded by twelve (110) planes, and octahedron-shaped, respectively. Particles with different morphologies are collected from different locations in the synthesis device, which indicates the temperature distribution and residence time affect structure of fabricated nanoparticles to some extent.

Silver nanoparticles were synthesized by DC arc thermal plasma successfully [94]. Silver nanoparticles are widely used in antimicrobial and electronics as a versatile material [95,96]. The plasma reactor consists of tungsten cathode and graphite crucible for holding metallic silver block. The fabricated sliver nanoparticles have a cubic (*fcc*) structure according to XRD spectrum. Crystallite size estimated by Scherer formula is around 25 nm. The TEM images reveal that there is no agglomerate condition in product and the size distribution is from 20 nm to 150 nm. This variation in diameter has a positive effect on thick film technology because the small particles can be used as "neck joints" for large particles.

There is an obvious increase in burn rate and detonation properties for Al particles with a size scale decrease from micro-scale to nano-scale [97]. In addition, passivation is an integral step for Al nanoparticle fabrication due to the reactivity of Al. Conventional method allows synthesized Al nanoparticles expose to air to slow oxidation to form thickness Al₂O₃ coating layer. However, this oxide layer impairs Al nanoparticle properties. Organic passivating layer can enhance powder properties in energetic system application [98]. Passivation Al nanoparticles with organic coating were fabricated by transferred arc thermal plasma [99]. The diameter of fabricated nanoparticles is around 27 nm, the oxide percentage decreases to 3% which is much lower than powder obtained from other methods. The organic layer is identified by FTIR analysis.

Multi-layer ceramic capacitors (MLCCs) play an important role in current society. Extensive application has already been achieved by Ni-base electrode-MLCC rather than Pd-base electrode MLCC. The volumetric capacitance which relates to stacking number and capacitive area of electrolyte layers is an index for MLCC property. The properties of Ni nanoparticles can affect above indices according to research [100]. Nickle nanoparticles were fabricated by inductivity coupled thermal plasma with different feeding rates and quenching rates successfully [101]. The raw material was selected as Ni(OH)₂ micro-powders with a mean size is 17 µm. Physical phase transition and chemical reaction occur simultaneously during plasma process. Fabricated nanoparticles show a tinier diameter with quenching gas injection with a mean value of 30 nm. The products show well spherical morphology without quenching gas.

The complex reaction environment results in lots of uncertainty during plasma process, especially for induction thermal plasma. The synthesis process is affected by particle number density, diameter and specific surface. Understanding more details of the synthesis process benefits nanoparticle synthesis and further application. Quenching gas flow rates and powder feed rates effect were investigated by numerical simulation, the Al, Ti, Au and Pt are selected as subjects [89,102]. These researches indicate that, for all metals, the enhanced quenching gas flow rates lead to particle number density and specific surface increase while the mean diameter decrease. Moreover, the higher powder feed rates cause larger mean diameter and smaller specific surface.

II. Alloy

Alloy nanoparticles evoke lots of interest because of their tunable optical, electronic and catalytic properties over a broad range by adjusting element composition [103]. Thermal plasma as an efficient fabrication method is applied to alloy nanoparticle synthesis.

Nano-scaled magnetic alloy is widely used as smart dampers, drug delivery vehicle, degradation catalyst, magnetic storage device and microwave shielding [104,105]. Magnetic property is sensitive to alloy composition. Iron nickel alloy nanoparticles with different iron percentages (from 25% to 75%) were synthesized by transferred DC arc thermal plasma [106]. Since nucleation and particle growth occur at high temperature, the disordered phase (*fcc*) γ -FeNi is obtained. Poor crystallinity is observed in Fe-rich nanoparticles. Diameter range of products from 20 nm to 40 based on TEM images. High crystallinity leads to high saturation magnetization and the best magnetic performance is shown in Fe_{0.5}Ni_{0.5}.

Another promising candidate for magnetic material is Fe-Co alloy which owns high saturation magnetization, large permeability, and low coercivity [107]. Conventional fabrication methods, such as polyol, thermal decomposition, and sol-gel, are difficult to wash the surfactants completely from the surface of as-synthesized nanoparticles. This situation impairs the magnetization per total mass [108]. Induction thermal plasma can improve this problem. A series of Fe-Co alloy nanoparticles have already been prepared by a new induction thermal plasma setup, namely, low oxygen induction thermal plasma. The new setup allows nanoparticle fabrication under inert gas atmosphere, further achieving direct synthesis of bare metal particles [109,110]. The experiment results show that the diameter of products is around 90 nm and all products present a low oxygen degree.

The unique superiorities of induction thermal plasma are attributed to novel alloy nanoparticle synthesis, especially appropriate to rare-earth alloy nanoparticle synthesis. The Sm-Co alloy was synthesized successfully by low oxygen induction thermal plasma as a permanent magnet material [111]. The property evaluation of permanent magnet material is based on remanent magnetization and coercivity, these indices are controlled by the microstructure of material. In addition, high coercivity can be achieved by particle diameter refinement [112]. The Sm-Co alloy can be used

as permanent magnet material according to the report, simultaneously, this alloy can acquire high coercivity by high anisotropy field of Sm-Co [113,114]. Micrometer scale raw material with molar ratio 5:1 was injected into Ar plasma. The synthesized nanoparticles have a spherical morphology and the mean size is 61 nm.

III. Oxide

Oxide nanoparticles, especially metal oxide nanoparticles, are attractive for a large variety of applications including bactericidal agents, catalysis, sensors, optoelectronic material, and environmental remediation [115–117]. There are various metal oxide nanoparticles have already been acquired by DC thermal plasma and RF induction thermal plasma.

Copper oxide nanoparticles show good antibacterial and have already been synthesized by thermal plasma [118]. Atomic compositions for Cu and O are calculated as 54.18% and 45.26% based on EDS results, respectively. This is because there are few Cu and Cu₂O nanoparticles existed as by-products. Prepared nanoparticles show a diameter range from 22.4 nm to 94.8 nm. The TEM images indicate the CuO nanoparticles have an approximate equi-axes shape with no sharp edges. Simultaneously, almost all particles have only one unique grain.

Nanosized alumina attracts attention ascribing to its application in engineering ceramics, catalysts, semiconductor packing materials and eco-materials. Aluminum powders were selected as raw material, nanosized Al₂O₃ particles were synthesized after Ar-O₂ RF induction thermal plasma processing [119]. Feed rate was fixed at 1667 mg/min and radial quenching gas was injected from shoulder of reactor. The experiment results demonstrate that smaller nanoparticles with narrower diameter distribution are synthesized by enhanced quenching gas flow rates. However, excessive quenching rates impair nanoparticle growth.

Titanium dioxide nanoparticles are known as function material and they are utilized in sun protection creams, textile fibers and wood preservatives, have already been synthesized by induction thermal plasma [62]. Ilmenite was selected as raw material because of its the low-price and easily obtain. The raw material is evaporated completely in high temperature area, then vapor phase reactions occur. The TiO and FeO vapor are synthesized at first, the TiO₂ and (FeO)₂(TiO₂) liquid are formed with the temperature decrease. These tiny droplets would be solidified in lower temperature region and finally form nanoparticles. Since the weight of TiO₂ nanoparticles is lighter than nanoparticles containing Fe, the particles collected from the top of chamber are considered TiO₂. The XRD spectra indicate the phase of products are anatase and rutile TiO₂.

Partially shielded 4*f*-orbital of rare earth oxides attracts much attention. Gate dielectrics and photo catalytic application lead to Nd₂O₃ nanoparticles being used in industry in order to improve the electrical properties [120]. Micro-sized Nd(OH)₃ powders were injected into center of Ar plasma plume by Ar. The XRD spectra indicate that the product is hexagonal Nd₂O₃. Morphology of products was detected by TEM and the images show the prepared nanoparticles exhibit a faceted morphology with good uniformity in size and shape. All particles are smaller than 100 nm and most particles are around 20 nm although the product has a wide diameter range.

IV. Nitride

Titanium nitride nanoparticles have a wide application in various regions, such as composition material production, nanostructured coating, mechanical property improvement of alloy and metal [121]. Nanosized TiN particles have already been synthesized by DC arc thermal plasma [122]. Single-phase TiN nanoparticles were obtained after sedimentation. Titanium hydride with size range from 1µm to 100 µm were injected into thermal plasma, nitrogen was used to generate plasma. Micro-sized and nano-sized particles are obtained simultaneously. Micro scale particles

contain TiN, Ti₆O and Ti based on XRD spectra. These particles have a laminar structure on surface. This resulted from the insufficient residence time of molten titanium nitrogenation. Nanosized particles show the single phase, identifying as TiN based on the XRD spectra. The experiment results also indicate that decreasing diameter of raw material would allow more TiN nanoparticles synthesis. The mean size of TiN nanoparticles is around 20 nm.

The iron-nitrogen system has been studied for a long time due to its remarkable mechanical and magnetic property. Recently, this research focuses on iron nitride nanoparticles because of the high saturation magnetization and high coercivity [123]. Moreover, the FeN nanoparticles are also used as the precursors for γ -FeN_x which has "giant magnetic moment" [124]. Iron nitrides nanoparticles were prepared by RF thermal plasma [125]. Iron powder with size lower than 10 μ m was injected into thermal plasma by Ar, argon and hydron were used as sheath gas to generate plasma. Nitrogen and ammonia were used as nitrogenization source. The results show there two phases exist in product, the α -phase and γ -phase present the 55 nm and 27 nm diameter, respectively.

Aluminum nitride nanoparticle attracts interest ascribing to its high intrinsic thermal conductivity, high electrical insulation and similar thermal expansion coefficient to silicon [126]. Purity of AlN nanoparticle is an important index for their property. Ratio frequency induction thermal plasma is an ideal method for fabrication of AlN nanoparticle with high purity because of the electrodeless discharge. Spherical Aluminum powder with $3 \sim 8 \ \mu m$ size distribution was selected as the raw material. Nitrogen was used as sheath gas and nitrogenization source. The experiment results reveal that AlN nanoparticles are synthesized successfully, while a few Al remains as by-product. The percentage of by-product would decrease with N₂ flow rate and input power increase, meanwhile, the reduced reaction pressure also benefits high purity of product.

V. Boride

Titanium boride nanoparticles have already been synthesized by RF induction thermal plasma successfully [127]. There is a wide application of titanium boride nanoparticles in physics, chemistry and engineering, including electromagnetic shielding, wear-resistant coating, solar control windows interaction with IR and UV lights. The TiB₂ nanoparticles show better properties than TiB based on the research [128]. However, the high melting point of raw material results in a dilemma about the synthesis of phase controlled TiB₂ nanoparticles with high purity using conventional methods. The high temperature and electrodeless discharge of RF induction thermal plasma provide an ideal method for TiB₂ nanoparticle fabrication. The difference between nucleation B and Ti leads to the feed rate becoming an important index. The mass fraction of TiB₂ decreases with feed rate increase in the boron-rich condition, while the boron-poor condition presents an opposite tendency.

The increasing demand for industrial applications in information storage, magnetic fluids and catalysts lead to the research interest in cobalt boride nanoparticles, in addition, cobalt borides also play a significant role in hydrogen storage and fuel cells [129]. Colloidal synthesis is a common method to obtain cobalt boride nanoparticles, however, there are still some challenges, such as the cleaning of liquid colloidal, complex operation, and high costly. Cobalt boride nanoparticles were synthesized by the RF induction thermal plasma with C/B mole ratio of 1, 2 and 3 [130]. The synthesized CoB and Co₂B nanoparticles have a diameter range from 18 nm to 22 nm. Enhanced feed rate leads to more CoB and Co₂B nanoparticles generation, meanwhile, this also leads to larger diameter of products.

Nickel boride and tungsten boride nanoparticles were also prepared by DC arc thermal plasma [131]. The former is regarded as an efficient catalyst for selection reduction of halides and nitro compounds [132]. The latter has a potential application in rock milling and mining because of its

superior hardness [133]. The experiment result demonstrates that exposure time in high temperature region affects crystallinity. Lower crystallinity is observed in nickel boride because the Ni has a lower nucleation temperature. While the higher nucleation temperature of W provides longer condensation time of W and B, further the higher crystallinity is achieved.

VI. Carbide

The high melting point, great hardness, good mechanical stability, and low work function allow ZrC nanoparticles to become an advanced ceramic and to apply in mechanical and nuclear industry [131,132]. Common fabrication methods, such as self-propagating high temperature synthesis, mechanical alloying and reaction sintering, cannot produce ultrafine powders with high purity. Nanosized ZrC particles were synthesized by RF induction thermal plasma successfully [135]. The ZrCl₄ was used as raw material. Sheath gas was a mixture of CH₄ and H₂, where CH₄ was also carbon source. Conversion rate of ZrC rises with H₂ flow rate increase, all synthesized nanoparticles smaller than 100 nm.

Titanium carbide nanoparticles were synthesized by induction thermal plasma [136]. The TiC nanoparticle is widely used for cutting tools, polishing paste, abrasive, and wear-resistance material because of its high melting point, high hardness, and good thermal conductivity [137,138]. Titanium dioxide is used as raw material for conventional synthesis methods for TiC nanoparticles. The product size is affected by raw material size to great extents, namely, nanosized TiC is synthesized by nanosized TiO₂. There is no such size limitation in thermal plasma synthesis. Carbon source and raw material were CH₄ and Ti powder, respectively. Experiment results indicate all TiC nanoparticles are smaller than 100 nm, enhanced input power benefits TiC synthesis. Simultaneously, the feed rate should be lower than 5 g/min and molar ratio of Ti/CH₄ should be set as 1.

Tungsten carbide is regarded as a candidate in refractory and anti-corrosion material ascribing to its high melting point, high hardness, and excellent wear resistance [139]. Simultaneously, it would show good catalyst property when size reduces to nanoscale [140]. It is difficult to obtain uniform size distribution particles using common methods, such as ball milling and spray conversion process. Tungsten carbide nanoparticles prepared by DC thermal plasma can improve above dilemma [141]. Multi-wall carbon nanotubes, amorphous carbon and CH₄ can be used as carbon source, the molar ratio of W/C was fixed at 2/3. The experiment results demonstrate that the main product is W₂C and WC, by-product is WC_{1-x}. The main product transforms from W₂C to WC_{1-x} with W/CH₄ molar ratio increase.

VII. Silicide

Metal silicide nanoparticles exhibit a wide application in electronic, magnetic, optical, catalyst and mechanical properties with different constitute metals, stoichiometries and crystal structures [142]. Since the high melting point of raw material, metal silicide nanoparticles are always synthesized by high-temperature methods [143]. Thermal plasma satisfies the high temperature demand completely. Formation mechanism of different metal silicide nanoparticles has already been studied computationally, four systems, Cr-Si, Co-Si, Ti-Si, and Mo-Si, were selected as the subjects [144,145]. The simulation results demonstrate that the product particle size is around 10 nm and the silicon content is related to nucleation and condensation phase.

Saturation pressure and precursor fraction effect on synthesized metal silicide nanoparticles were also studied computationally [114,146]. The small difference in saturation vapor pressure for metal and silicon can lead to a narrow range in composition because of the almost simultaneous co-condensation of metal and silicon. In addition, a huge gap in saturation vapor pressure results in a greater time lag for co-condensation for metal and silicon during particle

growth process. The greater time lag for co-condensation further results in a wide range of composition in product.

VII. Amorphous

Amorphous hydrogenated carbon nitride film is used as wear-resistant film for coating magnetic disks [147]. Common fabrication method is chemical vapor deposition. However, the film property is closely related to deposition processing. Power feed, gas pressure, gas flow rate, and substrate bias and temperature influence the final result to great extents [148]. The RF thermal plasma can improve above problems. Nitrogen and methane are used as N and C sources, respectively. Optical emission spectra indicate that the CN peak is observed in N₂-CH₄ plasma. Increasing N₂ in gas mixture can suppress C_mH_n species and enhance CN and CHN species. The experiment also reveals that CN and CNH species would not influence film growth directly.

Spherical particles of ternary metal oxide show lots of desirable application, such as photoluminescence, microwave application and optical property [149]. Amorphous alumosilicate nanoparticles with spherical morphology have already been prepared by RF thermal plasma [150]. Mixture of SiO₂, Al₂O₃ and KOH was injected into thermal plasma, the molar ratio of Si/Al and K/Al was fixed at 4 and 1, respectively. There is an obvious amorphous peak in XRD spectra, simultaneously, the crystalline peaks belonging to Al₂O₃ and SiO₂ are also detected. Composition of products was identified by EDS, showing that peaks of Al, Si, K and O were all detected. Spherical morphology of prepared particles was observed by TEM and SEM.

Amorphous Si nanoparticles are believed as a reliable strategy to improve cycling performance in lithium ion batteries due to volume variation. Microscale Si powder was fed into induction thermal plasma with 250 mg/min, argon used as counter quenching gas was injected into reaction chamber to enhance quenching rate during plasma process [151]. The XRD spectra reveal SiO₂

and crystalline Si are also synthesized as by-products besides amorphous Si. Amorphous degree increases with quenching gas flow rate increase, while the mean diameter of product shows an opposite tendency. Simultaneously, the agglomerate percentage also witnesses a growth with quenching gas flow rate increase.

Amorphous lithium compounds are treated as a candidate for solid electrolytes. The high lithium content is necessary in order to achieve high ion conductivity and energy density. Mechanical milling and sol-gel are common methods to obtain amorphous nanoparticles with high Li content. However, time-consuming and complex operation put a dilemma during fabrication process. Induction thermal plasma which is characterized by rapid quenching rate, large volume, and electrodeless discharge is considered an ideal method to prepare amorphous high Li content compounds with high purity.

Amorphous LiSiPON nanoparticles were fabricated by induction thermal plasma, particle spheroidization was achieved simultaneously [34]. Mixture of Li₂O, Si₃N₄, Li₄P₂O₇ and Li₄SiO₄ was injected into thermal plasma, argon and nitrogen was used to generate plasma. Stoichiometry of LiSiPON amorphous nanoparticles is investigated by EDS, confirming as Li_{2.8}Si_{0.8}P_{0.2}O_{2.5}N_{0.66}.

1.4 All-Solid-State Battery

There is an increasing demand for clean energy in current society because of the energy crisis and carbon neutrality. Electricity is a promising replacement for fuel owing to its high efficiency and environment friendly. Lithium ion battery is the most widely used storage device in industry and daily life. While the rapid development of electric vehicle and flammability of lithium ion battery urges the pursuit of high energy density and safe battery. Recently, the research point transforms to all-solid-state battery (ASSB) which all the battery material is solid state. Especially,

the electrolyte is solid state instead of liquid. The difference between Li ion battery and ASSB is presented in Fig. 1.5 (a).

The high energy density can be achieved by ASSB because of the solid state battery material in ASSB. The relationship between volumetric and gravimetric energy density for different batteries is shown in **Fig. 1.5 (b)**. Moreover, the Li ion battery also exists a serious safety issue. The lithium dendrites grown during cycling causes the short current of battery and finally results in an explosion. Moreover, liquid electrolyte would be decomposed over 300 K and release flammable gas. These limitations of liquid electrolyte lead to a narrow battery safety window that is lower than 4V. No leakage and non-flammable in ASSB allow the safety window to enlarge to 5V ascribing to the solid electrolytes. The safety window between the two types of battery is presented in **Fig. 1.6 (a)**. The superiorities of ASSB allow it to become an excellent selection for next generation battery.

1.4.1 Ion Transition Mechanism in Solid

Solid state leads to the ion transition mechanism in solid being totally different from liquid. The potential energy profile of mobile ions can be considered flat due to the uniform surrounding and the fast exchange between solvating molecules and solvent molecules. While the ion diffusion in solid needs to pass through bottleneck points which set an energy barrier. **Figure 1.6 (b)** shows the different potential energy profile in liquid and solid. The low energy barrier usually leads to high ionic mobility and ion conductivity. Hence, understanding the mechanism not only benefits improving the dilemma in current research but also promotes novel and efficient solid electrolyte development.

Fast ion conductor (FIC) is considered a candidate for solid electrolyte, because FIC maintains high ion conductivity over extended temperatures and chemical activities, simultaneously,

remains electronic insulating [152]. The FIC has high ionic conductivity and low activation energy below the melting point. There are two structural features of ion conductor: (1) highly ordered structure array, which can form tunnels, layers, or three-dimensional network localized on one of the ion sublattices; (2) highly disordered complementary sublattice, where the number of equivalent sites exceeds the number of available ions to fill them. Ion transition pathway plays a critical role in ion conductors based on the above features. Various solid electrolytes have already been fabricated following this critical rule, and the results indicate that there are two types of solid electrolytes roughly [153].

First type of solid electrolyte achieves ionic conductivity relies on point defects, including alkali and alkaline earth halides and some oxides. Ions only mobile among point defects in solids, such as vacancies or interstitial ions, this situation leads to an intrinsic conductivity associated with the point defect concentration. Simultaneously, extrinsic conductivity can be achieved by introducing impurities to create point defects in ionic or cationic sublattices. Extrinsic conductivity is related to the solid activation energy. Secondly, ion transit by disorder of sublattice of one of the ions, including α -AgI and β -Al₂O₃ [154]. Crystal lattice is constructed by one ionic species, many available energetically equivalent sites occur in mobile species sublattices.

I. Ion Conductivity in Solid

The ion conductivity can be expressed as **Eq. 1-8** with the assumption that the conduction occurs predominantly for a single ionic species:

$$\delta = n(Z_e)\mu \tag{1-8}$$

where *n* is the concentration of ion with charge Z_e and the mobility μ . A diffusion model is introduced in order to insight more details. The diffusion mode is characterized by isolated jump
with random walk of mobile species. Meanwhile, ions are visualized as vibrating within a potential well of energy E_m as a characteristic vibrational frequency v_0 . Assuming Boltzmann statistics, the diffusion constant D is given by:

$$D = \alpha d^2 v_0 \exp(-E_{\rm m}/kT) \tag{1-9}$$

where *d* is the ion jump distance, α is geometrical factor and k is Boltzmann constant, *T* is temperature. According to Nernst-Einstein equation, mobility μ can be expressed as:

$$\mu = \frac{Z_e D}{kT} \tag{1-10}$$

so, the ion conductivity is given by:

$$\delta = \frac{n(Z_e)^2 \alpha d^2 v_0}{kT} \exp(-E_m/kT)$$
(1-11)

which shows temperature-depended ion conductivity following Arrhenius equation as found in solid conductors.

The structure defects are the nonnegligible ion passage, the most conventional ion conductors rely on this passage. In addition, the ion concentration depends on the defect formation. Schottky defect (cation-anion vacancy pair) and Frenkel defect (cation or anion vacancy-interstitial pair) are two major defects for ion conductor, and **Fig. 1.7 (a)** is the illustration of mainly structure defects in solid. In either case, the defect concentration, namely the mobile ion concentration, is given by:

$$n = n_0 \exp(-E_d/kT) \tag{1-12}$$

where E_d is 1/2 defect-pair formation energy, n_0 is the ion total amount. The fraction of mobile ion can be written as n/n_0 . Since the value of E_d is usually large, while the value of n/n_0 is quite small. Thus, the ion conductivity is given by:

$$\delta = \frac{n_0 (Z_e)^2 \alpha d^2 v_0}{kT} \exp((E_m + E_d)/kT)$$
(1-13)

$$= \frac{n_0 (Z_e)^2 \alpha \beta d^2 v_0}{kT} \exp(-E_m/kT)$$
(1-14)

where β is the value of n/n_0 .

II. Ion Transition Mechanism in Crystalline

The ion conductivity is strongly related to crystal defects, such as point defects, line defects, planar defects and volume defects. Since point defects are the most closely associated property according to experiment results, the transition mechanism is discussed based on point defects. **Figure 1.7 (b)** displays the schematic diagram of ion migration mechanism in solid. Carrier type, diffusion pathway and diffusion type are three factors that govern the ion transition mechanism in crystalline solid [155]. The classical microscopic approach of ion transition is a famous diffusion model in ionic crystals adapted by Stevel. This mode makes a point that the cations moment is random with the isolated jumping from one Coulombic well to another.

There are four typical crystal structures that show high ion conductivity. The crystal that has a γ -Li₃PO₄ framework structure is considered a promising candidate for solid electrolyte, reaching ion conductivity as high as 1.6×10^{-4} S/cm at room temperature [156]. This crystal usually experiences a phase transition ($\gamma \rightarrow \beta \rightarrow \alpha$) with temperature increase, the ion transition is related to the tetrahedron arrangement which affects cations position [157]. These three inequivalent cation positions occur with phase transition from γ to β , which results in the cation sublattice disorder. Meanwhile, the tetrahedrons in β -phase present a zig-zag arrangement which allow cations to locate in tetrahedron and octahedron, further promoting interstitial cation diffusion and finally achieving ion transition.

The second structure is characterized by rhombohedral unit cell consisting of corner-shared tetrahedron and octahedron. Two octahedrons and three tetrahedrons share one oxygen atom and form a lantern structure, which builds a three-dimension network structure. A cation pathway is formed by this structure and cations are mobile in solid. The ion conductivity is not very high in

this crystalline structure, while in isovalent or aliovalent substitution of some element, such as Ti, the enhanced conductivity reaches as high as 1.0×10^{-3} S/cm at room temperature [158].

Crystalline with a perovskite structure ABX₃ shows a high potential application in solid electrolyte. This structure has a cubic unit cell consisting of A-ion at corner, B-ion at center and oxygen at the face-center. The coordination number of A-ion and B-ion is 12 and 6 respectively, they are corner-shared with each other. Smaller cation introductions would change Li and vacancies concentration simultaneously. Concentration and interaction of vacancies allow the ordering of Li or vacancies in the planes perpendicular to *c*-axis. Lithium ions are mobile in *ab* plane by those vacancies. Large rare-earth or alkaline-earth metal ion in A site can increase ion conductivity [159,160].

The last type is garnet crystal who possesses a general chemical formula of $A_3B_2(XO_4)_3$ and a face-centered cubic structure. Coordination number for A, B and X is 8, 6 and 4, respectively. Cation is located in both tetrahedron and distorted octahedron in this structure. Moreover, there is also a phase transition with temperature increase. The high temperature phase shows a higher ion conductivity because it always has a disordered cation sublattice and a three-dimension network structure formed by face-shared tetrahedron and octahedron.

III. Ion Transition Mechanism in Amorphous

Ion conductivity is affected by several factors, such as the mobile carrier concentration, based on **Eq. 1-13**. However, the total disorder structure of amorphous results in difficultly to specify these factors. Because the surrounding environment of the same type of ion in amorphous is likely different, a single characteristic migration energy or attempt frequency cannot be found, those properties should be expressed by distribution. The measured value is considered as either the average value or the highest potential barrier that the ions encounter during diffusion.

Plenty of attention has already been conducted and an assumption is put forward [153]. All of the alkali ions are treated as mobile ions, because each ion is surrounded by many nearly equivalent vacancies which allow ion migration. Those vacancies build the ion pathway. In addition, some researchers think those alkali ions should be dissociated from their original site linked to non-bridge oxygen (NBO) before the migration, and the ion jumps from one NBO to another NBO [161]. It is difficult to define the point defect because a defect can only exist in relation to an ordered structure for amorphous. Thereby, the above model is often regarded as Frenkel disorder which is a character of glass.

Warburg discovered the nature of cationic conductivity in 1884 and showed that good conductivity is obtained in the system consisting of alkali ions (Li, Na or K) and glass former oxides (SiO₂, B₂O₃ and P₂O₅). Those systems present similar ion conduct in crystalline with lattice defects with the following characters. Amorphous also has exclusive conductivity which is caused by lattice disorder or introduced impurities but the value is always low. Electrons are limited by the low coherence length which results from potential fluctuation caused by disorder. Those amorphous occupies low activation energy from 1 to 0.5 eV which promises the higher ion conductivity contrasted to crystalline. Summarizing and comparing the experiment results with crystalline, researchers think that amorphous has a same indirect interstitial mechanism of ion diffusion to crystalline, namely, the ions mobile in amorphous is relying on a pathway built by structure disorder [162].

The ion conductivity of amorphous is depended on the nature and concentration of its composition. The ion conductivity of silicate and borate glass increases with alkali ion concentration increase owning to the activation energy decline. Meanwhile, the larger alkali ion would lead to the higher activation energy, further reducing the ion conductivity [152]. Because

the strain energy is risen to squeeze larger alkali ion by restricted opening in amorphous. Divalent alkali ion addition would result in higher activation energy and lower conductivity.

1.4.2 Material for All-Solid-State Battery

All battery material is solid state in ASSB, this is the largest discrepancy with conventional lithium ion battery. The strong interfacial resistance between solid electrode and electrolyte caused by the poor connection impairs the ion transition to great extents although there are no side reactions of solid electrolyte dissociation, which reduce cycling life-span and poor performance [163]. Therefore, the ASSB material research concentrates on improving interfacial connection and enhancing energy density.

I. Anode Material

Lithium metal is considered a promising anode material for ASSB because of its high specific capacity and low electrochemical energy [164]. Meanwhile, the inorganic solid electrolytes utilization can avoid leakage and flammability [165]. While lithium dendrites would be formed during the cycling, resulting in the lithiation/delithiation amount decline [166]. The short current would occur when the current is over the critical current density of electrolyte [167]. Above situations are caused by the insufficient interfacial contact between Li anode and solid electrolyte. The high electronic conductivity also results in those problems [168]. In addition, lithium metal can react with H₂O, O₂, and CO₂ in atmosphere, which causes a challenge for storage and assembly. Artificial protection layer between Li anode and solid electrolyte is introduced to improve this dilemma. Various layers are investigated, such as Li₂CO₃, Al₂O₃, Li₂O, and Li_xSiS_y, the Li anode becomes more stable in air after the artificial layer utilization [169–172].

Addition of other metals to Li anode to form alloy anode is one method to improve Li anode property. Because the anode material based on electrochemical alloy reaction allows Li ion to move inside the anode material rather than concentrating on the surface, providing a more stable interface between electrolyte and anode [173]. There are two types of electrochemical alloy reactions, one is the reconstitution reaction and the other is solid-solution reaction [174]. The former would experience a phase transition which results in additional activation energy. Much less structure change during solid-solution reaction, which allows reaction to occur with a low charge-discharge voltage hysteresis at a potential close to Li/Li⁺ redox couple [175]. The general formula of alloy anode material is Li_xM, where M can be Si, Sn, Mg, Ag, and so on. Until now various Li alloy anode materials have already been prepared [174,176,177].

Carbon group anode materials are an important series for ASSB anode. Carbon materials such as graphite show a low potential and a charge/discharge efficiency of over 90%, simultaneously, it also has a layer structure that can allow Li ion insertion and extraction. However, the theoretical capacity of around 372 mAh/g is too low to satisfy large devices [178,179]. The SiS₂-based glass solid electrolyte is not compatible with graphite anode during the experiment [180]. Another candidate in carbon group is the Si anode, the high gravimetric capacity, low voltage window, low price, and abundance lead to Si being considered an ideal material both in science and industry [181]. While the pulverization of Si anode caused by the volume change during cycling and unstable interface limits its application, coating artificial layer and double-wall nanotube utilization are proven to improve these problems [182,183].

II. Cathode Material

The cathode material of ASSB is usually a composite electrode. The cathode consists of electrode active material, solid electrolyte, and conductive agent which is used for ion and

electron transition. However, the inevitable interface also affects cathode properties negatively as mentioned above.

The oxides, such as LiCoO₂, LiFePO₄, and LiMnO₂, are put in high hopes and used as promising cathodes due to high electrode potential [184,185]. A space-charge layer is formed between solid electrolyte and cathode. Sulfide-based material is always selected as the solid electrolyte because of its high ion conductivity. Since the massive discrepancy of chemical potential between sulfide and oxide, the Li ion would transit from electrolyte to electrode which causes the Li ion to be depleted of electrolytes interface and a space-charge layer is formed. Moreover, the such space-charge layer would be strengthened when cathode material is mixedconduct oxide, namely, the oxide also achieves electron conduct besides ion conduct. The spacecharge layer on cathode can vanished by decreasing the Li concentration gradient between cathode and electrolyte. The concentration gradient of Li ion can be resolved by the electron conduct, further achieving the equilibrium of Li ion transiting from electrolyte to cathode additionally, finally, the enlarged space-charge layer of electrolyte would be formed [186].

Introducing thin oxide film which is characterized by ion conduction and electrode insulation to cathode surface was proven to prevent space-charge layer efficiency. This thin film forms two interfaces, one is the interface between cathode and introduced layer. This interface can reduce space-charge layer because there is a small difference in chemical potential between two oxides. Another is the interface between solid electrolyte and introduced layer, the space-charge layer is also suppressed owing to electron insulation. Various oxide artificial thin films have already been developed, such as Li₄Ti₅O₂, LiNbO₃, and Li₃BO₃, these experiment results indicate that the electrochemical property of ASSB is enhanced [186–188].

Continuous research is conducted to obtain high-performance cathode material aiming to improve electrochemical properties of ASSB. The $LiNi_xCo_yMn_zO_2$ (NCM, with x+y+z=1) is

developed as a promising cathode material in industry application. There are several ratios for three elements, such as NCM 433 (x:y:z=4:3:3), NCM 532, NCM 622, and NCM 822 [189]. Compared to conventional oxide cathode, the NCM occupies a high energy density (>200 mAh/g at 4.3-4.6 eV) [190]. The fixable ratio and synergistic effect of three elements lead to NCM being compatible with Ni, Co, and Mn advantages simultaneously. Nickel ions are used as electroactive species and provide higher capacity, cobalt ions enhance rate performance and processing ability and Mn ions with 4⁺ valence can maintain structure stability [191].

III. Electrolyte Material

Sulfide and oxide are two main candidates for solid electrolytes. Various solid electrolytes with different compositions and structures have already been obtained by different fabrication methods. **Figure 1.8** is the summary of ionic conductivity of different solid electrolytes. Sulfide occupies relatively high Li ion conductivity compared to oxide. In addition, amorphous electrolytes show better electrochemical property than crystalline. Here, the following introduction focuses on crystalline electrolytes, amorphous will be introduced in next section with more details.

Sulfide electrolytes present a high ion conductivity at room temperature. Various sulfide electrolytes were synthesized, such as Li₂S-GeS₂, Li₂S-GeS₂-ZnS, and Li₂S-GeS₂-Ga₂S₃ systems [192]. The similarity among those sulfides is the γ -Li₃PO₄-type structure. This structure is characterized by oxides tetrahedrons and LiO₆ octahedrons [193]. There are six candidates for above systems, they are Li₂GeS₃, Li₄GeS₄, Li₂ZnGeS₄, Li_{4-2x}ZnGeS₄, Li₅GaS₄, and Li_{4+x+δ}(Ge_{1-δ'-x}Ga_x)S₄, respectively [194]. Ion conductivity as high as 6.5 × 10⁻⁵ S/cm at room temperature was obtained for Li_{4+x+δ}(Ge_{1-δ'-x}Ga_x)S₄. Meanwhile, the property of ASSB assembled by Li_{4+x+δ}(Ge_{1-δ'-x}Ga_x)S₄/LiCoO₂ was also investigated, the battery was charged/discharged from 0.5 V to 4.2 V at a constant current in 13-64 µA/cm² range at room temperature. Lithium silicon sulfides system is

another candidate for crystalline sulfide electrolytes. Compounds belonging to this system also have a γ -Li₃PO₄-type structure. The ion conductivity would be enhanced when Li ion interstitials or Li ion vacancies are created by partial substitution of other cations. The solid solution Li_{4-x}Si₁₋ _xP_xS₄ (x=0.6) presents an excellent ion conductivity of 6.4×10⁻⁴ S/cm at room temperature with negligible electronic conductivity [195].

A serious problem that cannot be ignored in sulfide electrolytes is the poor chemical and electrochemical stability. This disadvantage causes the harmful gas H₂S generation during cycling, which further impairs performance of battery. Oxide attracts great attention owing to its good chemical and electrochemical stability. Various oxide solid electrolytes were fabricated. While the low ion conductivity (around $10^{-6} \sim 10^{-8}$ S/cm) at room temperature makes a huge challenge. Aiming to solve this problem different novel structure oxide electrolytes are synthesized.

The first reported oxide about LISICON-type electrolyte is $Li_{12}Zn(GeO_4)_4$ which shows ion conductivity as high as 1.25×10^{-1} S/cm at 573 K. Two factors are proposed in ion conductor, first one is the size of bottlenecks between neighboring Li ion position, the second one is the bonding energy between mobile Li ion and network anion O²⁻ [196]. The network is constructed by $[Li_{11}Zn(GeO_4)_4]^{3-}$ for $Li_{12}Zn(GeO_4)_4$ and other free Li ion can diffuse between interstitial positions. New LISICON-type electrolytes $Li_{10.42}Si_{1.5}P_{1.5}Cl_{0.08}O_{11.92}$ and $Li_{10.42}Ge_{1.5}P_{1.5}Cl_{0.08}O_{11.92}$ which partially doped O²⁻ with Cl⁻ was synthesized aiming to obtain higher ion conductivity. The above electrolytes show ion conductivity of 1.03×10^{-5} S/cm and 3.7×10^{-5} S/cm at room temperature, respectively [197]. Moreover, $Li_4Al_{1/3}Si_{1/6}Ge_{1/6}P_{1/3}O_4$ is predicted has ion conductivity of 9×10^{-4} S/cm based on MD simulation [198].

Perovskite-type oxide electrolytes are always written as LLTO due to the first reported compound is $Li_{3x}La_{2/3-x}TiO_3$. Lithium and La ions are in the center, titanium ions occupy the corners in perovskite-type electrolytes. The $Li_{3x}La_{2/3-x}TiO_3$ presents a bulk ion conductivity of

 1×10^{-3} S/cm and an ion conductivity of over 2×10^{-5} S/cm at room temperature [199]. The modified perovskite-type electrolyte was reported that has higher ion conductivity than the originals. The Li_{3/8}Sr_{7/16}Ta_{3/4}Zr_{1/4}O₃(LSTZ) was found that the highest ion conductivity of 2×10^{-4} S/cm and 1.33 $\times 10^{-4}$ S/cm for bulk and grain boundary respectively at room temperature [200].

Another important oxide electrolyte is garnet-type electrolyte which is first reported with the composition of Li₃Ln₃M₂O₁₂(M = Te, W; Ln = Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). Different elements in electrolyte display various lattice constant. The ion conductivity is affected by the stability of octahedron [201]. The Li₃Ln₃M₂O₁₂ has a lower ion conductivity of around 10^{-6} S/cm at room temperature. Doping strategy is introduced in order to enhance ion conductivity. Barium-doped Li₆BaLa₂Ta₂O₁₂ shows an ion conductivity of 4.0×10^{-5} S/cm [202]. Gallium-substituted Li_{6.55}Ga_{0.15}La₃Zr₂O₁₂ which was prepared in dried O₂ atmosphere shows excellent ion conductivity as high as 1.3×10^{-3} S/cm at 297 K and 2.2×10^{-3} S/cm at 315 K [203].

1.5 Research on Amorphous Electrolyte

Amorphous solids are considered to have optional high ion conductivity based on ion transform mechanism in solid, because they have more structure point defects and minimization of the grainboundary effect. Moreover, amorphous nanoparticles also present unique advantages in processability, stability, and tunability [204]. Since the larger specific surface area of amorphous nanoparticles benefits reducing interfacial resistance, declining amorphous particle size to nanoscale is considered a research hotspot.

1.5.1 Conventional Amorphous Fabrication Methods

The disorder and chaotic structure of amorphous material lead to its fabrication method being totally different from crystalline. Because the structure of amorphous material is similar to liquid,

how to maintain this structure in solid state becomes important. Lots of attempts are tried in order to achieve these goals, melting quenching is a common method. Sol-gel method and mechanical milling are also developed with the technology process.

I. Sol-gel Method

The first attempt at inorganic ceramic and glass was fabricated by sol-gel method as early as the mid-1800s. Ebelman and Graham observed that SiO₂ glass was obtained by hydrolysis of tetraethyl orthosilicate and Si(OC₂H₅)₄ under acidic condition [205]. The lower processing temperature, high homogeneity and purity of target material, and possibility of various forming processing allow sol-gel method to become an ideal method for glass fabrication [206–208]. Binary systems ZrO₂-SiO₂, SiO₂-P₂O₅ glass, complex composition system SiO₂-P₂O₅-CaO-Ag₂O, SiO₂-P₂O₅-CaO-MgO-Na₂O-K₂O glass have already been synthesized successfully by sol-gel method [209–212].

II. Mechanical Milling Method

Mechanical milling is considered a method for stabilizing nonequilibrium phase. Amorphization of solid-state is a common utilization of mechanical milling. The milling process is a defect accumulation process, the increase of energy would cause the loss of stability [213,214]. Meanwhile, the material amorphous systems have different composition ranges for amorphous synthesis, the composition range can be modified by changing milling conditions, such as milling intensity [215,216]. Mechanical milling is widely applied to amorphous fabrication, especially for the system that is difficult to form into glass. Alloy glass is an important region, such as Fe-W, Cr-C, and Ag-Pa [217–219]. High Li content compounds are also difficult to form into

amorphous, glass-ceramic Li₇P₂S₈I, amorphous Li₂Si₂O₅, and novel LiTi₂(PO₄)₃ glass-ceramic nanoparticles are acquired successfully by this method [220–222].

III. Melt Quenching Method

The melt quenching technology is widely used in glass and glass-ceramic production. Compared to sol-gel method melt quenching consumes less time while requiring higher operation temperature. This technique is developed by Duwez and his collaborators in the 1960s, the high cooling rate can reach 10^6 to 10^5 K/s [223]. The high purity raw material (99.9%) is same stoichiometric as target material. The raw material is milled to mix sufficiently before heating. The melt can be quenched in the atmosphere on a cooper plate. The quenched glass flake is annealed at 773 K in order to remove the internal stress [224]. The products synthesized by melt quenching present a plate morphology. Lots of glass with different functions are successfully synthesized. Amorphous sulfide electrolyte Li₂S-P₂S₅ with high ion conductivity, glasses of GeSbSe, SLS-ZnO have already been obtained [225–227]. In addition, melt quenching method is available to bioactivity material SiO₂-BaO-ZnO-B₂O₃-Al₂O₃ glass and SiO₂-B₂O₃-AO-La₂O₃ (A = Sr, Ba) glass [228,229].

1.5.2 Amorphous Lithium Sulfide

Sulfide electrolytes have high ion conductivity even at room temperature as previous mentioned. Amorphous sulfide electrolytes occupy higher ion conductivity in contrast to crystalline. The lithium thiophosphate (LPS) is the most studied sulfide system. The first-time report about high conductivity of LPS is in the late 1970s, the researcher found that doping lithium halides (LiBr, LiI) can rise LPS glass conductivity to a great extent [230]. Increased ion conductivity is found with the P_xS_y unit transiting from di-tetrahedron $P_2S_7^4$ to tetrahedron PS_4^3 -

with different Li₂S to P₂S₅ molar ratios. Simultaneously, the declined active energy is observed in increased non-bridge sulfur atoms [231]. However, it is not that the higher Li content the better. There is a limitation of Li₂S to P₂S₅ molar ratio. Non-conducting Li₂S crystal would be generated in amorphous material when Li₂S:P₂S₅ ratio increases to 4:1, which results in the barrier for Li diffusion. Various LPS solid electrolytes have already been fabricated. The Li₃PS₄ glass who was prepared by wet-chemical method shows an anomalous high conductivity of around 1.64×10^{-4} S/cm [156]. The 70Li₂S-30P₂S₅ glass was prepared by quenching melts achieving high ion conductivity of 2.1×10^{-3} S/cm, which can replace liquid electrolytes directly [232]. The glass-ceramic of Li₂S-P₂S₅-LiN which is prepared by mechanical milling owns conductivity around 1.4×10^{-3} S/cm [233].

The Li₂S-GeS₂-Ga₂S₃ system glass solid electrolyte was also prepared with limited compositions. The composition ranges of glass formation are <10% or 40%-60% of 1/2 Li₂S with small amounts of Ga₂S₃. The highest ion conductivity was 1.4×10^{-4} S/cm [234]. Unfortunately, the Ge atom would compromise the chemical compatibility of LPS with Li metal [235]. Since silicon is another typical glass former, the Li₂S-SiS₂ system glass electrolyte was also prepared. Over 2×10^{-3} S/cm ion conductivity was achieved in $60Li_2S-40SiS_2$ [236].

1.5.3 Amorphous Lithium Phosphate Oxynitride

Serious Li-penetration problem is observed when electrolytes connect with metallic lithium anodes, which further results in interfacial compatibility problems. Lithium phosphate oxynitride (LiPON) was introduced because of its remarkable resistance to Li-penetration owing to the low electronic conductivity [237]. However, its ion conductivity is low around 10⁻⁶ S/cm at room temperature. In the 1990s, the amorphous LiPON was reported first time [238,239]. The LiPON is considered to consist of randomly oriented, corner-shared PO_{4-y}N_y tetrahedron, the lithium

atoms are distributed randomly within the interstices of network. The most common fabrication method for LiPON is ratio frequency magnetron sputtering.

Lots of research have been developed aiming to enhance ion conductivity at room temperature. These researches indicate that conductivity benefits from former disorder [240]. Substitution of nitrogen, silicon, or boron on oxygen sites can enhance the structure disorder, further enhancing ion conductivity [241,242]. Electronegativity decrease of the system is achieved by anionic substitution, simultaneously, non-bridge specie is also enhanced in material, which reduces the required energy for interstitial Li mobility. Another method to improve conductivity is adding excessive Li, which increases the percentage of available interstitial Li, thereby, obtaining higher conductivity [243].

1.5.4 Amorphous Lithium Oxide

Amorphous sulfide electrolytes not only generate harmful gas H₂S during cycling but also cannot avoid lithium dendrite growth as previous introduction. Above serious problems make that new material development becomes an urgent issue. Lithium oxide electrolytes stand out among all candidates owing to their impressive chemical and electrochemical stability. Amorphous oxide electrolytes become the research focus in the next stage combing the ion transform mechanism in solid with stability issues. Diverse system electrolytes which contain common glass former have already been synthesized by conventional amorphous fabrication methods.

I. Amorphous Lithium Phosphate System

Electrochemical properties of $50Li_2O-(50-x)P_2O_5-xAl_2O_3$ amorphous electrolyte were also investigated [244]. A series of glass was prepared by melting quenching method. The ion conductivity shows a non-linear change with Al_2O_3 content increase, the maximum is obtained at

6.25% of Al₂O₃ around 3.4×10^{-7} S/cm at 323 K and 3.9×10^{-4} S/cm at 573 K, respectively. Meanwhile, the experiment also indicates a structure change with different Al₂O₃ content is related to the conductivity change. The molar volume presents a decreased tendency with Al₂O₃ increase from 0 to 6.25%, then increases with Al₂O₃ continuously increase. Conductivity would rise with density increase, with a peak of 6.25% Al₂O₃ in density, while it also descent due to the available interstitial volume [245].

Nanoscale glassy powder Li₂O-Al₂O₃-TiO₂-P₂O₅ (LATP) was synthesized by melting quenching method and mechanical milling [246,247]. The LATP nanoparticles have high conductivity of 10^{-3} S/cm at room temperature. The LATP consists of MO₆ octahedrons and PO₄ tetrahedrons which link with each other by corner-sharing to form a 3D network structure. Lithium ions located in 6-fold O octahedron are responsible for mobile, being located in 10-fold O coordination are favorable for chemical stability of electrolytes besides being mobile. The sample, Li_{1.4}Al_{0.4}Ti_{1.6}(PO₄)₃, was synthesized by mechanical milling, displaying the highest conductivity of 1.09×10^{-3} S/cm with activation energy of 0.28 eV at room temperature.

The ion conductivity of amorphous lithium phosphate was also investigated based on thermodynamic modeling of their chemical structure[248]. The calculated results demonstrated that the ion conductivity increase with Li_2O percentage increase due to more non-bridge oxygen bonds formation. These non-bridge oxygen bonds thermally activate hopping between negatively charged positions, further leading to higher ion conductivity [249]. The calculated results have a similar increased tendency with experimental results in ion conductivity, although the value is higher than experiments. This situation can be explained by the arrangement of lithium coordination polyhedrons LiO_n (n=4 or 5) in a sort of percolation channels where the last would be linked through O-Li-O.

II. Amorphous Lithium Silicate System

Amorphous electrolytes of the Li₂O-P₂O₅-SiO₂ system were prepared by sol-gel method. Different molar ratio products show different ion conductivity. The lower conductivity is obtained at 573 K while high value is achieved at 289 K for all products, which mostly owing to protonic conduction at room temperature. Moreover, increasing Li and P content also attributes to Li conductivity. Selected samples, $10Li_2O-25P_2O_5-65SiO_2$, show conductivity as high as 2×10^{-3} S/cm at room temperature [250].

The complex silicate-based amorphous electrolyte $Li_2O-K_2O-Al_2O_3-SiO_2$ was also systematically studied [251]. Addition of V_2O_5 to $Li_2O-K_2O-Al_2O_3-SiO_2$ can increase mechanical properties, chemical resistance and thermal stability [252]. The ion conductivity increases with V_2O_5 content increase although Li_2O content decrease. Simultaneously, the ion conductivity presents a high value at high temperature than low temperature. Topological order of the amorphous silicate-based electrolyte was investigated aiming to understand this phenomenon by MD simulation. The ratio of NBO/BO experiences a rising tendency with V increase. The average jump distance of Li ion is small at low temperature, which results in the less connection of conduction channels. The V plays as the network former at low V content while playing as a channel former at high content. The connection of ion conduction channel can be enhanced by the V-channel, and high Li conduction is achieved.

Molecular dynamic was utilized to simulate the ion pathway in amorphous lithium silicate electrolyte [253]. The increased Li content leads to higher ion conductivity due to the enhanced density and connectivity of pathway for the motion of Li⁺ in the amorphous. The high Li content allows the volume fraction of pathway cluster to be increased, meaning the local pathway dimensional becomes higher in Li-rich condition.

III. Amorphous Lithium Borate System

Amorphous lithium borate-based electrolyte attracts lots of interest because boron is a typical network former. The Li₂O–SeO₂–B₂O₃ amorphous electrolytes were prepared by melt quenching and characterized by various analysis methods [254]. The maximum conductivity was observed in the 50% Li₂O condition. The typical mixed-former effect was responsible for the increased ion conductivity. The SeO₂ acts as a network former in SeO₂-rich composition and provides another ion pathway, which allows the higher Li ion mobility.

Lithium ion conducting glass of $Li_2O-B_2O_3$ -SiO₂ was prepared by melt quenching, the maximum of conductivity was acquired with $50Li_2O-38B_2O_3-12SiO_2$ glass sample around 2 × 10^{-6} S/cm [255]. The ion conductivity strongly relies on the Li_2O content. The glass formation region in ternary $Li_2O-B_2O_3$ -SiO₂ system can be extended when the ratio of SiO₂/B₂O₃ decreases to 0.3. The viscosity and crystallization tendency are decreased by addition of B₂O₃.

The local structure of lithium borate glass was also studied by high resolution solid state NMR same as other lithium oxide system glass [256]. The ion conductivity increases with Li ion addition due to the number of ion carrier increasing, simultaneously, the BO₃ unit gradually transforms to BO₄⁻. This tendency conforms to Arrhenius behavior characterized by thermally activated transport. However, the generation of NBO with Li continuous addition would impair Li mobility by the interaction and result in declined conductivity.

IV. Amorphous Lithium Titanate System

Perovskite-type Li_{3x}La_{2/3-x}TiO₃ (LLTO) evokes lots of interesting ascribing to high ion conductivity, however, crystalline LLTO is not stable when connect to Li metal because Ti⁴⁺ is reduced to Ti³⁺, further results in high electronic conductivity [257]. Amorphous LLTO can solve this problem and maintain high conductivity simultaneously. Amorphous LLTO was prepared by

sol-gel method [258]. The conductivity is 4.5×10^{-6} S/cm, 6.9×10^{-6} S/cm, 1.3×10^{-5} S/cm and 3.8×10^{-5} S/cm at 303 K, 323 K, 343 K and 363 K, respectively. This growth tendency indicates amorphous LLTO stability over a wide temperature range. Activation energy over this temperature range is fixed at 0.36 eV.

1.6 Objective and Contents

Amorphous oxide nanoparticles with high Li content are promising candidates for solid electrolytes, researching high-performance and novel lithium oxide nanoparticles contributes to ASSB development and application. The sufficient structure defects of amorphous promise Li ion mobility, which has a positive effect on ion conductivity. Enhanced formability is acquired when the size of amorphous particles decreases to nanoscale. Since the chemical and physical properties of amorphous independent of direction, isotropic ion conductivity can be achieved. In addition, the large specific surface area of amorphous nanoparticles promotes the connection between electrolyte and electrode, further reducing the strong interfacial resistance. However, the limitation of conventional synthesis methods results in a dilemma in solid electrolyte research. Hence, it is urgent and necessary to search for an efficient and advanced synthesis method for amorphous oxide nanoparticles with high Li content.

Induction thermal plasma is considered an excellent method for amorphous nanoparticle synthesis owing to its unique superiorities. The extremely high temperature (up to 10^4 K) allows raw material to decompose and vaporize immediately after injecting into thermal plasma. The rapid quenching rate (10^3 - 10^6 K/s) can prevent orderly growth, and form into amorphous structure. In addition, counter-flow quenching gas utilization can further increase quenching rate. Electroless discharge of induction thermal plasma avoids the pollution from electrodes, which allows products to achieve high purity. Therefore, the objective of this dissertation is synthesis of

amorphous lithium oxide nanoparticles with different systems and investigation of formation mechanism. Amorphous Li₃BO₃, Li₄GeO₄, and Li₅AlO₄ were selected as target material based on the following reason. Boron, germanium, and aluminum can function as glass former to construct the skeleton of amorphous. High Li content offers more ion carriers to ensure high ion conductivity to satisfy the requirement of electrolytes. The low glass transition temperature allows the amorphous structure to more easily form during the rapid quenching process. The amorphous LiPO₃ and Li₄SiO₄ nanoparticles have been synthesized by induction thermal plasma in our laboratory. The amorphous Li₂O-B₂O₃-P₂O₅ and Li₂O-B₂O₃-SiO₂ nanoparticles were also considered as the target material before the experiment. This mixed glass former effect is considered to investigate in the future work.

Figure 1.9 shows the flow diagram of this dissertation, and the contents in each chapter will be presented briefly in this section.

In chapter 2, amorphous Li_3BO_3 nanoparticles were synthesized by induction thermal plasma with different Ar/O_2 molar ratios in sheath gas, different Ar and O_2 quenching gas flow rates. Formation mechanism of lithium borate was investigated after analyzing thermodynamic equilibrium and experiment results. Particle growth process during plasma process was understood to clarify the formation mechanism of amorphous nanoparticles. The effects of O_2 and quenching gas flow rate on the amorphous degree and chemical composition were discussed based on borate unit transformation and temperature distribution.

In chapter 3, amorphous Li₄GeO₄ nanoparticles were synthesized by induction thermal plasma. The experiment was conducted by different Ar/O₂ molar ratios in sheath gas, different Li/Ge molar ratios in raw material, different carrier gas and quenching gas flow rates. Formation mechanism of lithium germanate was studied based on experiment results and thermodynamic analysis. The saturation ratio of different phases was utilized to understand the chemical

composition variation. The Ge content and quenching rate effect were discussed according to the topological order of products.

In chapter 4, amorphous Li₅AlO₄ nanoparticles were synthesized by induction thermal plasma under the experiment conditions of different Li/Al molar ratios in raw material and quenching gas flow rates. Formation mechanism of lithium aluminate was understood by combining the experiment results with thermodynamic analysis. Aluminate polyhedron and Al coordination number were introduced to elucidate amorphous degree tendency. The effects of Li content in raw material and quenching gas flow rate were discussed based on O/Al molar ratios and aluminate polyhedrons transformation.

In chapter 5, the formation ability of amorphous nanoparticles with high Li content was studied based on comparing experiment results of Li-B-O, Li-Ge-O and Li-Al-O systems. The formation ability was discussed from product structure and chemical composition. The formation ability was summarized relying on bond strength, time lag of co-condensation and structure unit transformation.

In chapter 6, the conclusion was summarized and future works were put forward to improve the research.

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Fig. 1.1. The domains of plasma as the function of temperature and electron density [259].



Fig. 1.2. The typical ranges of electron temperature rang with electron density for non-equilibrium and equilibrium plasma [260].



Fig. 1.3. Schematic diagrams for different generators of thermal plasma. (a) transfer DC arc, (b) non-transfer DC arc, (c) free-burning arc, (d) multiphase AC arc, (e) induction thermal plasma, (f) microwave thermal plasma [261,262].



Fig. 1.4. Process of nanoparticles synthesized by thermal plasma [263].



Gravimetric energy density / Wh kg-1

Fig. 1.5. The discrepancy between Li ion battery and all-solid-state battery. (a) schematic diagram of structure for two types of batteries, (b) volumetric and gravimetric energy density for different batteries [264].



Fig. 1.6 The discrepancy for Li ion and all-solid-state battery (a) the range of safety window, (b) the potential energy.



Fig. 1.7. Schematic diagram of (a) structure defects and (b) ion migration mechanism.



Fig. 1.8. Lithium ionic conductivity for different solid electrolyte materials [264].



Fig. 1.9. Flow diagram of this dissertation.

2. Synthesis of Amorphous Li₃BO₃ Nanoparticles

The ASSBs attract academic attention gradually and strongly with rapid development of electric vehicles and portable devices. The unique advantages of ASSBs, such as large energy density, no leakage and non-flammable, allow them to become a promising choice for second-generation batteries [1]. The solid-state battery materials of ASSBs promise a higher lithium transport number and wider electrochemical window, however, also result in lower lithium ion conductivity and stronger interfacial resistance between electrolyte and electrode, contrasted to conventional lithium ion batteries [2]. The investigation of solid electrolyte materials has been a hot issue in order to address the above problems.

Amorphous Li₃BO₃ nanoparticles are considered a promising candidate for solid electrolytes ascribing to their outstanding advantages. The chemical and electrochemical stability of oxide avoids electrolyte decomposition and harmful gas generation during cycling. Amorphous structure increases the formability, simultaneously, the sufficient defects of amorphous benefit Li ion mobility. The interface area between electrode and electrolyte can be enhanced by the nanosized particles, which decrease the interfacial resistance. The high Li content in Li₃BO₃ promises the high ion conductivity, as well as, the good glass former boron allows easy formation of amorphous nanoparticles.

The conventional synthesis methods of amorphous nanoparticles, such as mechanical milling and sol-gel method, are time-consuming and operation-complex. Advanced and efficient synthesis methods should be developed as soon as possible. Induction thermal plasma is considered an ideal method to generate nanoparticles with high purity due to its distinctive advantages, such as extremely high temperature up to 10⁴ K, rapid quenching rate (10³-10⁶ K/s) and controllable atmosphere (oxide, reduction, or inert). Besides, the electrodeless discharge, large plasma volume, and low gas velocity also ensure its superiority in nanoparticle synthesis [3,4]. Especially the rapid quenching rate is suitable for amorphous structure nanoparticle formation. Moreover, the nanoparticles can be synthesized in a very short time.

Therefore, this chapter focuses on synthesizing amorphous Li₃BO₃ nanoparticles by induction thermal plasma with different experiment conditions. The effect of O₂ flow rate, additional quenching gas and formation mechanism were investigated based on experiment results and thermodynamic analysis.

2.1 Experimental

2.1.1 Experimental Configuration and Procedure

Figure 2.1 shows a schematic illustration of experimental device for amorphous Li₃BO₃ nanoparticles synthesis. The setup mainly consists of power supply, powder feeder, plasma touch, reaction chamber, quench tube, and prepared particles collection filter. The thermal plasma was generated with 4 MHz applied electromagnetic field, and the input power fixed at 20 kW. Sheath gas was set at 60 L/min with different Ar (purity > 99.99%, Fukuoka Oxygen Cooperation) and O_2 (purity > 99.5%, Fukuoka Oxygen Cooperation) ratios. Argon was selected as quenching gas and was injected into chamber by quench tube which was placed 15 cm below touch. Oxygen offers oxidizing atmosphere for Li oxidation during plasma process. The injection of counter quenching gas offers rapid quenching rate. Other experiment conditions are listed in **Table 2.1**.

Crystal α -Li₃BO₃ was selected as raw material (diameter 10-30 μ m purity 99.9%, Toyoshima manufacturing.) was injected into reaction chamber through Ar at 600 mg/min. The raw material would be evaporated immediately in high temperature region after injecting into plasma, then the particles would nucleate in relative lower temperature region under supersaturated state. The product nanoparticle would be collected from the wall of chamber and filter after co-condensation,

coagulation. Oxygen was injected into chamber gradually after plasma process in order to ensure all lithium exists as compounds to prevent simple substance Li existence.

2.1.2 Analysis Method

The phase and crystal structure identification of prepared particles were achieved by X-ray diffraction (XRD, Rigaku Multifle), operating with a Cu K α source ($\lambda = 0.1541$ nm). The continue scan was conducted in a 2 θ range of 10°-90° at a scan speed of 1°/min. The borate structure and their relative amounts were understood by a microscopic laser Raman spectrometer (Raman, LabRAM ARAMIS). The wavelength of laser source in this research was 532 nm. The morphology of prepared particles was characterized through transmission electron microscopy (TEM, JEOL JEM-2100HCKM). The surface component of product was determined by X-ray photoelectron spectroscopy (XPS, Shimadzu KRATOS AXIS ULTRA) to check by product.

2.2. Experiment Results

2.2.1 Effect of Oxygen Flow Rate

The morphology of products synthesized by different O_2 flow rates was understood through TEM. The TEM photographs with electron diffraction are shown in **Fig. 2.2 (a)-(d)**. The TEM was operated at an acceleration voltage of 200 kV. A 16 mega pixel CMOS camera is used to capture digital TEM photographs. The diameter of the area of the electron diffraction is 200 nm. The spherical particles are only observed in O_2 1L/min condition, the agglomerates are observed in other conditions. The spherical particles would be produced at high temperature because of coalescence. The loose agglomerates with quite open structure would be formed at lower temperature. Those partially sintered particles form into non-spherical state at intermediate condition [5]. Induction thermal plasma is characterized rapid quenching rate. Generation of the lithium borate would be started in relative lower temperature region around 1700 K. Coalescence of lithium borate particles is negligibly slow, the agglomerates would form in this research. **Figure 2.2 (e)-(f)** is the enlarged TEM photograph of nanoparticles synthesized 2.5 L/min and 5 L/min O₂. The photographs indicate that the diameter of nanoparticles is around 30-50 nm indexed by red circle. Some particles indexed by orange circle have a diameter below 10 nm.

Figure 2.3 (a) shows the XRD spectra for products synthesized by different O₂ flow rates. Peaks of major product belong to high temperature phase Li₃BO₃ (β-Li₃BO₃) in all cases [6,7], the peaks of Li₂CO₃ are also detected as the by-products. The β-Li₃BO₃ is not stable at room temperature, and it would transit to thermodynamically stable phase (α -Li₃BO₃) around 977 K [8]. This structure could be remained owing to the rapid quenching rate in thermal plasma. The intensity of β-Li₃BO₃ peaks becomes weak with O₂ flow rate increase.

The estimated amorphous degree of product with different O_2 flow rates is shown in **Fig. 2.4**. The amorphous degree was estimated by *JADE* 6.5 (Material Data, USA) based on XRD spectra using the following equations:

$$W_{Amorphous} = 1 - DOC$$
(2.1)

$$DOC = \frac{I_c}{I_t}$$
(2.2)

where DOC represents degree of crystalline, I_c and I_t are crystalline integral intensity and total integral intensity, respectively. There is an obvious growth in amorphous degree with O₂ flow rate increase from 1 L/min to 2.5 L/min to 5 L/min, the corresponding estimated amorphous degree are 54%, 59%, and 70%. Increased amorphous degree is caused by the different composition and structure of different products. The reason for difference among products in composition and structure would be discussed in next section.

The Raman analysis was conducted to understand amorphous part composition. Figure 2.5 (a) is the Raman spectra for products synthesized by different O_2 flow rates. The wavelength of laser

was fixed at 532 nm. Gray dots line is the experimental spectrum, the blue line is the cumulative fitting. The characteristic peaks are fitted by Gaussian function and four typical peaks are identified. The peaks located around 760-785 cm⁻¹, 850-830 cm⁻¹, and 950-930 cm⁻¹ are indexed to borate units [9]. These three regions are indexed to diborate ($B_4O_9^{6-}$) in red dotted line, pryoborate ($B_2O_5^{4-}$) in orange and orthoborate (BO_3^{3-}) in purple, respectively. The peak around 1100 cm⁻¹ is classified as CO_3^{2-} in green [10]. Besides target material Li₃BO₃ other lithium borates Li₆B₄O₉ and Li₄B₂O₅ were also synthesized during the plasma process according to Raman spectra. The Li₄B₂O₅ is not stable at room temperature, and it decomposes into Li₆B₄O₉ and Li₃BO₃ below 923 K [11]. The Li₄B₂O₅ could be remained ascribing to the rapid quenching rate.

The relative molar amount of each structure group was estimated in order to obtain the relative amount of target material. The relative amount of a particular structure group can be estimated assuming that the total number of Raman scattering events gives rise to the area under the peak [12]. In addition, the integral intensity of each Raman peaks is related to the molar amount of the corresponding borate structure unit. The relative molar percentage of each unit could be accessed based on above assumption [13]. **Figure 2.6** displays the evolution of the relative amount of each borate group and CO_3^{2-} in product synthesized by different O_2 flow rates. The percentage of BO_3^{3-} is dominant compared to other units in product. There is a downward trend in BO_3^{3-} percentage with O_2 flow rate increase, while the other structure group in product show an opposite trend. The $B_4O_9^{6-}$ and $B_2O_5^{4-}$ are more easily form into amorphous structure contrasted to BO_3^{3-} at same quenching rate owing to bridging oxygens (BOs) existence. Therefore, the higher amorphous degree was achieved with the O_2 flow rate increase due to more $Li_6B_4O_9$ and $Li_4B_2O_5$ generated.

Figure 2.4 shows the estimated result for amorphous Li_3BO_3 degree with different O_2 flow rates. This result was obtained based on following considerations. The Raman spectra indicate the products consisted of $Li_6B_4O_9$, $Li_4B_2O_5$, Li_3BO_3 , and Li_2CO_3 . Only Li_2CO_3 and β - Li_3BO_3 peaks

were detected by XRD, which means the amorphous part in product consisted of Li₆B₄O₉, Li₄B₂O₅ and part of Li₃BO₃. The relative amount of amorphous Li₃BO₃ could be estimated by subtracting the relative amount of Li₆B₄O₉ and Li₄B₂O₅ from all amorphous part. **Figure 2.4** demonstrates the percentage of amorphous structure Li₃BO₃ increases with O₂ flow rate increase. Around 33% of amorphous Li₃BO₃ was obtained in 1 L/min case. The amorphous Li₃BO₃ degree increases to 37% and 41% in 2.5 L/min and 5 L/min cases, respectively.

The by-product Li₂CO₃ was detected in final product, although no carbon source was input during plasma process. The generation of Li₂CO₃ is considered after the plasma process, that is, those unreacted Li₂O attach H₂O and CO₂ in atmosphere to form Li₂CO₃. The surface composition of product was identified by XPS in order to verify this hypothesis. **Figure 2.7 (a)-(b)** show the XPS spectra for B (1s) and C (1s) with different O₂ flow rates. The peak near 188 eV and 191 eV are assigned to carbide and B-O bond, respectively [14]. Peaks position of carbide is located near 282 eV and 284 eV as for carbon (1s) [15]. The other two peaks near 286 eV and 289 eV are classified as C-O, the two peaks identify the existence of CO_3^{2-} [15]. There is a great difference in penetration depth for Raman and XPS analysis methods [16]. The XPS can measure the kinetic energy and quantity of escape electrons from 1 nm to 10nm below the surface of the material, while the penetration depth of Raman is around 1000 nm under the analysis condition used in this research [17]. Thus, XPS and Raman focus on the surface region and whole particles, respectively.

Figure 2.8 is the estimated result for relative molar amounts of C in products based on Raman and XPS with different O_2 flow rates. The figure demonstrates that the relative molar amount of C on surface is much higher than whole particles. This huge gap reveals that the carbon in products concentrates on the surface. Surface of the product has the possibility to contact the atmosphere, further reacting with H₂O and CO₂ to form Li₂CO₃. Hence, the aforementioned hypothesis is verified, the CO₂ is the carbon source of Li₂CO₃ synthesis. The existence of Li₂CO₃ also indicates that Li₂O is synthesized and that not all Li₂O take part in the reaction during the plasma process.

The above experiment results indicate that O_2 has a positive effect on amorphous Li₃BO₃ fabrication. Meanwhile, the O_2 injection results in more by-product generation. The by-product Li₂CO₃ concentrates on the surface of the produce. The reason would be discussed in the next section.

2.2.2 Effect of Argon Quenching Gas

There is no significant difference among products synthesized by different quenching gas flow rates in morphology. No spherical particles were observed and the products present agglomerate state. Because the quenching rate is enhanced by quenching gas. There is no sufficient energy to support the boundary of those small particles to eliminate to form a new spherical particle in low temperature region.

The major product in crystal part is also β -Li₃BO₃ in different quenching gas flow rates, the Li₂CO₃ was detected as by-product. The XRD spectra are presented in **Fig. 2.3 (b)**. The estimated amorphous degree of products is shown in **Fig. 2.9**. The result reveals that the amorphous degree increases obviously after quenching gas utilization, arriving at around 71% in 40 L/min quenching gas condition. This phenomenon is related to nanoparticle growth and the chemical composition of the product. Details would be discussed in the next section.

The products synthesized by different quenching gas flow rates also consisted of Li_3BO_3 , $Li_4B_2O_5$, $Li_6B_4O_9$, and Li_2CO_3 based on Raman analysis. The Raman spectra are presented in **Fig. 2.5 (b)**. The quantified result of Raman spectra is shown in **Fig. 2.10**. There is a similar tendency in quenching gas condition with O_2 condition. The percentage of BO_3^{3-} shows a declining trend, while other borate groups and CO_3^{2-} present a rising trend with quenching gas flow rates increase. Enhanced amorphous degree of product was obtained due to more $Li_6B_4O_9$ and $Li_4B_2O_5$

generation. The amorphous Li₃BO₃ degree result is presented in **Fig. 2.9**. The result demonstrates more amorphous Li₃BO₃ was fabricated after quenching gas utilization, occupying around 42% of the final product in 40 L/min condition.

The by-product Li₂CO₃ formation mechanism has already been discussed in the previous part. The XPS results for quenching gas condition show Li₂CO₃ also concentrate on the surface of products. The Li₂CO₃ was synthesized by unreacted Li₂O with H₂O and CO₂ in atmosphere.

The above results indicate that Ar counter quenching gas influences Li₃BO₃ generation negatively. Synthesis of amorphous Li₃BO₃ is promoted by quenching gas. The reason would be discussed in the next section.

2.2.3 Effect of Oxygen Quenching Gas

Diatomic gas O_2 was selected as another quenching gas in order to investigate the effect of different types of quenching gas. Figure 2.3 (c) displays the XRD spectra of products synthesized by different O_2 quenching gas flow rates. A declined tendency of crystal peak intensity was observed with O_2 quenching gas flow rate increasing. Another by-product LiOH·H₂O was detected in 20 L/min case. There is no hydrogen source injection during the plasma process, simultaneously, not all Li₂O take part in reactions. These LiOH·H₂O are considered to be synthesized by unreacted Li₂O with H₂O in the atmosphere. Estimated amorphous degree of products reaches around 72% with 40 L/min O_2 flow rates, shown in Fig. 2.11.

The products synthesized by different O_2 quenching gas flow rates are also consisted of Li₃BO₃, Li₄B₂O₅, Li₆B₄O₉, and Li₂CO₃ based on Raman analysis, the Raman spectra are shown in **Fig. 2.5** (c). The quantified results of Raman spectra are shown in **Fig. 2.12**, this result demonstrates composition variety tendency of products synthesized by different O₂ quenching gas flow rates is similar to Ar quenching gas. The percentage of BO₃³⁻ decrease from 53% to 43% with O₂

increasing to 40 L/min. Amorphous Li₃BO₃ degree is presented in **Fig. 2.11**, showing around 43% amorphous Li₃BO₃ nanoparticles are obtained with 40 L/min O₂ quenching gas injection.

The above results indicate that quenching gas type cannot affect the synthesized compounds and amorphous degree in Li-B-O system. Because the temperature of injected O_2 is similar to injected Ar, both of them are close to room temperature. The thermal conductivity of Ar and O_2 at room temperature is similar, which leads to no obvious discrepancy in the temperature distribution. Thus, there are no comparable experiment results in different types of quenching gas cases.

2.3. Discussion

2.3.1 Formation Mechanism of Lithium Borate Nanoparticles

There is a huge difference between induction thermal plasma and other conventional methods in amorphous nanoparticle fabrication regarding the formation mechanism. The lithium borate nanoparticles formation mechanism was investigated. This investigation attributes to understanding the effect of O_2 and quenching gas on product in composition and structure theoretically. The formation mechanism of nanoparticles in induction thermal plasma has already been investigated systematically [18–20]. The raw materials evaporate totally in high temperature region after injecting into plasma immediately, then particles nucleate in super saturated state in lower temperature downstream region, finally particles generation after condensation [20]. The reactions are ended by the solidification of each species in Li-B-O system. Particles grow continually through coagulation once occur in vapor phase. Therefore, the nucleation phase should identify first in the Li-B-O system. Because the solid interface is absent during the nucleation for thermal plasma synthesis. Homogeneous nucleation rate *J* is estimated based on non-dimensional surface tension in this paper and expressed as [21]:

$$J = \frac{\beta_{ij} n_s^2 S}{12} \sqrt{\frac{\Theta}{2\pi}} \exp\left[\Theta - \frac{4\Theta^3}{27(\ln S)^2}\right]$$
(2.3)

where S is saturation ratio, n_s is equilibrium saturation monomer concentration at temperature T. The saturation ratio is given by the following equation:

$$S = \frac{P}{P_{\rm S}} \tag{2.4}$$

where P and P_s represents partial pressure of vapor and saturation pressure, respectively. The nondimensional surface tension Θ is given by:

$$\Theta = \frac{\sigma s_1}{kT} \tag{2.5}$$

where δ is the surface tension, s_1 is the monomer surface area, k means Boltzmann constant. β_{ij} is the collision frequency function between monomers and expressed as:

$$\beta_{ij} = \left(\frac{3\nu_1}{4\pi}\right)^{1/6} \sqrt{\frac{6kT}{\rho_P} \left(\frac{1}{i} + \frac{1}{j}\right)} \times \left(i^{1/3} + j^{1/3}\right)^2$$
(2.6)

here, ρ_p means particles mass density and v_1 means monomer volume, *i* and *j* are equal to 1 because of the monomer collision mode of this method.

The particle formation could be experimental observation conveniently when the nucleate rate is over 1 cm⁻³ s⁻¹ [43]. The value of the corresponding saturation ratio is defined as the critical saturation ratio at nucleation temperature. The parameters of nucleation rate are the functions of temperature according to the above equations. Thereby, nucleation temperature is considered as the temperature at which the nucleation rate achieves 1 cm⁻³ s⁻¹. The nucleation temperature for B and Li estimated based on **Eqs. (2.3)-(2.6)** are 2998 K and 1056 K with 600 mg/min feeding rate, respectively. Melting points of oxides are regarded as nucleation temperature due to the two temperatures being always close and lacking physical properties. The relationship between nucleation temperature and melting point is presented in **Fig. 2.13**. **Figure 2.13** indicates that boron has the highest nucleation temperature and should nucleate first in this system. The melting point and boiling point in **Fig. 2.13** are obtained from Lang's Handbook of Chemistry [22].

The homogenous nucleation is also dependent on saturation ratio strongly beside the nucleation temperature. The vapor phase reactions among substances before nucleation would influence their vapor pressure to a great extent. Since thermal plasma is considered as thermodynamic equilibrium, the vapor phase reactions are chemical equilibrium. Thermal equilibrium composition in Li-B-O system is developed using thermodynamic calculation software FactSage 7.2 (Centre for Research in Computational Thermochemistry, Canada; GTT-Technology, Germany) with following conditions. The feeding rate of crystalline Li₃BO₃ is 600 mg/min, O₂ flow rate is 2.5 L/min. Since the nuclei cannot stably exist in high temperature region, the nucleation and condensation phase are solidified below 1000 K. The thermodynamic equilibrium composition is estimated with a temperature range of 1000-5000 K. The estimated result is shown in Fig. 2.14. The result reveals that O, Li, and BO vapor are dominant over 3000 K. The amount of B vapor is much lower around its nucleation temperature, which means insufficient B vapor pressure cannot lead to super saturation state. Thus, boron cannot nucleate first in Li-B-O system. The amount of O, Li and BO vapor lose their advantage gradually with temperature declining. Vapor of Li₂O and Li₂O₂ begin to rise, vapor of LiBO₂ becomes the stable phase in this system. The main reactions during this process are presented following:

$$B(g) + O(g) \rightarrow BO(g)$$
$$Li(g) + O(g) \rightarrow LiO(g)$$
$$BO(g) + LiO(g) \rightarrow LiBO_2(g)$$
$$LiO(g) + Li(g) \rightarrow Li_2O(g)$$

Figure 2.13 indicates that Li₂O would nucleate around 1711 K following B. The vapor pressure of Li₂O vapor is sufficient according to thermodynamic analysis. Hence, Li₂O would nucleate first in Li-B-O system. The Li₂O and LiBO₂ are the co-condensation phase.

The formation mechanism is put forward according to thermodynamic consideration. **Figure 2.15** presents the amorphous Li-B-O nanoparticles generation process. Crystalline Li_3BO_3 decomposes and evaporates into Li, B, and O vapor after injecting into thermal plasma in high temperature region. The vapor-phase reactions start among various substances to generate Li₂O vapor and LiBO₂ vapor. More and more Li₂O molecules are generated continuously to produce embryos. Simultaneously, the saturation vapor pressure decreases rapidly due to temperature decline. Homogeneous nucleation of Li₂O would start under super saturation state when temperature declines to 1711 K. Vapor of LiBO₂ and Li₂O heterogeneous co-condense on the Li₂O nucleus to form Li-B-O system particles subsequently. The driving force for heterogeneous condensation is saturation ratio *S*. Vapor of Li₂O achieves the supersaturated state earlier than vapor of LiBO₂, the Li₂O condensation would be dominant in initial stage [23]. The Li-rich nanoparticles of Li₃BO₃ are formed mainly at the early stage of particle growth. Another condensation phase LiBO₂ achieves super saturation state with temperature decrease. Vapor of Li₂O is consumed simultaneously. The B-rich particles of Li₆B₄O₉ and Li₄B₂O₃ would be formed in following stage.

There is an intense relationship between the structure of borate group and Li⁺ content. **Figure 2.16** illustrates the process for borate group transformation with Li⁺ increase. The borate structure transforms from six-member with one BO₄ tetrahedron (BO²⁻) to diborate (B₄O₉⁶⁻) to pyroborate (B₂O₅⁴⁻) to orthoborate (BO₃³⁻) in order with Li⁺ content increase [13]. The structure of BO₂⁻ starts to change when LiBO₂ and Li₂O vapor condense on Li₂O nuclei during the heterogeneous co-condensation process. The bridge oxygens (BOs) bonds start to break because the stronger electropositive of Li contrasted to B. The non-bridge oxygens (NBOs) start to generate. Vapor of Li₂O more rapidly condenses on the nucleus than LiBO₂ vapor at the early stage, the Li₃BO₃ is

synthesized by complete borate transition. This transition is impaired in the following stage because less Li₂O vapor takes part in the transition process. Hence, Li₃BO₃ was mainly synthesized at early stage due to the complete borate group transition. The Li₆B₄O₉ and Li₄B₂O₅ were mainly synthesized at following stage due to uncomplete transition caused by low Li₂O partial pressure.

The borate transition terminates by species solidification in the Li-B-O system. Every species of the Li-B-O system solidifies below 1000 K based on **Fig. 2.14** and phase diagram [11]. These synthesized particles grow continuously by coagulation in lower temperature region to form loose agglomerates. The temperature during coagulation process is not enough to provide sufficient energy to activate the surface of synthesized particles. Spherical particles cannot be formed by incomplete coalescence [24].

Borate transition is related to temperature distribution intensively because the process would be ended by solidification of species. Since diatomic O_2 releases heat through decomposition and ionization, while monoatomic gas Ar release heat only through ionization. The thermal conductivity of the Ar and O_2 mixture would be increased by adding diatomic gas O_2 into sheath gas. Therefore, addition of O_2 not only leads to improving heat transfer from plasma to particles but also shrinks the plasma flow [25,26]. Enhanced quenching rate in reactor chamber would achieve by the shrunken plasma flow. Since the counter-flow quenching gas suppresses high temperature region, the more rapid quenching rate is also achieved. The quenching rate would increase from 3.2×10^4 K/s without quenching gas to 1.3×10^5 K/s and 4.0×10^5 K/s after 20 L/min and 40 L/min quenching gas injection, respectively [27]. Hence, addition of O_2 into sheath gas and counter-flow quenching gas utilization could achieve steeper temperature gradient. The steeper temperature gradient accelerates temperature decrease and shortens co-condensation time. Solidification of species in the Li-B-O system is also promoted, the borate structure

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transformation also would be impeded. More $B_4O_9^{6-}$ remained in final product due to no sufficient transformation time. In addition, the more rapid quenching rate prevents $B_2O_5^{4-}$ decomposes into $B_4O_9^{6-}$ and BO_3^{3-} . This situation also reduces Li₃BO₃ amount. Therefore, less Li₃BO₃ was obtained in higher O₂ and quenching gas conditions. Increase of unreacted Li₂O leads to more Li₂CO₃ generation after plasma process.

2.3.2 Formation Mechanism of Amorphous Li₃BO₃

Nanoparticles synthesis by induction thermal plasma is an extremely fast and complex heat/mass transfer process. The whole process, containing phase conversion, interaction among thermofluid field, induced electromagnetic field, particles concentration field with numerous variables as well as chemical reactions, lasts only a few tens of milliseconds [28,29]. Therefore, nanoparticle formation and crystallization are considered to occur simultaneously during the process.

Figures 2.4 and **2.9** demonstrate the percentage of amorphous structure Li_3BO_3 increases with O_2 and Ar quenching gas flow rate increase. There is a significant influence of nanoparticle growth on temperature distribution. Because the critical indices during this process, such as morphology and structure of product, are influenced by temperature. Saturation ratio, *S*, is the driving force for nucleation based on **Eq. (2.3)**, the higher-level saturation ratio would lead to faster nucleation., Nucleation rate would be enhanced when *P* is fixed while P_s becomes lower. P_s is a function of temperature and the value would be lower when temperature decrease. The number of nuclei is increased at the more rapid quenching rate. Because the total amount of Li_2O vapor is constant, the vapor consumption of each nucleus would reduce with increased number of nuclei. This situation allows smaller particles to generate. The particle order growth time is also reduced owing to steeper temperature gradient. Moreover, particle growth is also impaired by the lower kinetic

energy. The lower temperature results in the lower kinetic energy of particles, which would further impair co-condensation and coagulation. Those small particles cannot achieve long-range order structure, and the product keeps the more chaotic state. Therefore, increased amount of amorphous Li₃BO₃ particles were obtained with steeper temperature gradient.

2.4. Conclusion

Amorphous Li₃BO₃ as solid electrolyte was synthesized successfully by induction thermal plasma with different O₂ flow rates and counter Ar quenching gas injection. The formation mechanism was investigated based on nucleation temperature and thermodynamic analysis. Enhanced quenching rate could reduce co-condensation duration time, further influence borate group transition negatively, and finally Li₃BO₃ percentage is decreased. More Li₆B₄O₉ and Li₄B₂O₅ are generated as amorphous structure, which enhances products amorphous degree. The enhanced quenching rate allows smaller size nuclei generation and prevents particles grow orderly. This phenomenon leads to more amorphous Li₃BO₃ production. In addition, the insufficient temperature caused by rapid quenching rate results in the product with agglomerated state.

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Parameter	Condition
Input power [kW]	20
Pressure [kPa]	101.3
Frequency [MHz]	4
Sheath gas rate [L/min]	60 (Ar+O ₂)
Inner gas rate [L/min]	5 (Ar)
Carrier gas rate [L/min]	3 (Ar)
Quenching gas rate [L/min]	0, 20, 40 (Ar) 0, 20, 40 (O ₂)
Feed rate [mg/min]	600
Ar/O ₂ molar ratio [-]	59:1,57.5:2.5, 55:5

 Table 2.1. Experimental conditions for induction thermal plasma system.



Fig. 2.1. Schematic diagram of amorphous Li₃BO₃ synthesized by induction thermal plasma.



Fig. 2.2. TEM photographs of products synthesized by (a) 1 L/min O₂, (b) 2.5 L/min O₂, (c) 5 L/min O₂. The red square is the focus of the electron beam on product. The corresponding diffraction pattern is shown in (d). The enlarged TEM photograph of nanoparticles synthesized (e) 2.5 L/min and (f) 5 L/min O₂.



Fig. 2.3. XRD spectra of products synthesized by different (a) O₂ flow rates, (b) Ar quenching gas flow rates and (c) O₂ quenching gas flow rates. Circle, triangle and square represent β-Li₃BO₃, Li₂CO₃ and LiOH·H₂O, respectively.



Fig. 2.4. Estimated amorphous degree of products and Li₃BO₃ synthesized by different O₂ flow rates. The error bars represent the standard errors of the corresponding average.


Fig. 2.5. Raman spectra of products synthesized by different (a) O₂ flow rates, (b) Ar quenching gas flow rates and (c) O₂ quenching gas flow rates. Gray dots line is the experimental results, the blue line is the cumulative fitting.



Fig. 2.6. The relative amounts of different groups in products synthesized by different O₂ flow rates. The error bars represent the standard errors of the corresponding average.



Fig. 2.7. XPS spectra of the products synthesized by different O₂ flow rates. (a) boron (1s) and (b) carbon (1s).



Fig. 2.8. Relative amounts of C in products estimated based on Raman and XPS with different O_2 flow rates.



Fig. 2.9. Estimated amorphous degree of products and Li₃BO₃ synthesized by different Ar quenching gas flow rates. The error bars represent the standard errors of the corresponding average.



Fig. 2.10. The relative amounts of different groups in products synthesized by different Ar quenching gas flow rates. The error bars represent the standard errors of the corresponding average.



Fig. 2.11. Estimated amorphous degree of products and Li₃BO₃ synthesized by different O₂ quenching gas flow rates. The error bars represent the standard errors of the corresponding average.



Fig. 2.12. The relative amounts of different groups in products synthesized by different O₂ quenching gas flow rates. The error bars represent the standard errors of the corresponding average.



Fig. 2.13. The melting, boiling, and nucleation temperature relationship for B, Li and oxides.



Fig. 2.14. Thermal equilibrium of the Li-B-O system: Li: B: $O_2 = 3:1.5:115$.



Fig. 2.15. Formation mechanism of Li-B-O powder by induction thermal plasma.



Fig. 2.16. Borate structure transformation process with Li⁺ percentage increase.

3. Synthesis of Amorphous Li₄GeO₄ Nanoparticles

Solid electrolytes act as the Li ion transition bridge between anode and cathode, playing a critical role in cycling performance, operation temperature region, and life span of ASSBs [1]. Three main requirements were put forward for solid electrolytes: i) a high degree of disorder to allow ion mobile; ii) a high concentration of weakly bonded Li ion; iii) a suitable structure that allows macroscopic motion of Li ion with low activation energy [2]. Amorphous solid electrolytes known for the total disorder structure were introduced to satisfy the above requirements. Moreover, the isotropic Li ion conductivity in amorphous electrolytes is also beneficial to the application due to the minimization of the grain-boundary effect [3]. Low electronic conductivity is another significant requirement for solid electrolytes. The decreased overlap of electronic states of neighboring ions can be achieved by the disorder amorphous structure, further leading to reduced electron mobility and enhanced ionic transference number [4]. Overall, amorphous structure is a promising factor for solid electrolytes.

The amorphous Li_4GeO_4 was selected as the target material according to the following reasons. Germanium is a good glass former ascribing to the covalent bonds to promise amorphous structure generation. Meanwhile, the high Li content of Li_4GeO_4 ensures high Li ionic conductivity.

This chapter focuses on synthesizing amorphous Li_4GeO_4 nanoparticles by induction thermal plasma with different Li/Ge molar ratios, O_2 flow rates, and carrier gas and quenching gas flow rates. The effect of Ge percentage, O_2 flow rate, quenching rate, and formation mechanism were investigated based on experiment results and thermodynamic analysis.

3.1. Experimental

3.1.1 Experimental Configuration and Procedure

The experiment device consists of power supply, powder feeder, plasma touch, reaction chamber, quench tube, and collection filter, the schematic diagram is presented in **Fig. 3.1**. The experiments were operated under atmosphere pressure. The frequency of applied electromagnetic field was 4 MHz and the input power was fixed at 20 kW. The sheath gas consisted of Ar (purity > 99.9%, Fukuoka Oxygen) and O₂ (purity > 99.5%, Fukuoka Oxygen) with various molar ratios. Total flow rate was adjusted at 60 L/min. The quench tube was located 15 cm below the torch. Argon was selected as quenching gas injected into the reaction chamber by the quench tube with different flow rates. Oxygen was injected into chamber with 3 L/min after plasma process and lasted two minutes to ensure all lithium exist as compounds in products.

Raw material is the mixture of Li₂CO₃ (purity 99%, Honjo Chemical Corporation) and GeO₂ (purity 99.99%, Kojundo Chemical Laboratory) with different Li/Ge molar ratios. The raw material was injected into plasma torch at 300 mg/min. The Li/Ge and Ar/O₂ molar ratio were fixed at 4:1 and 57.5:2.5 in the experiments of carrier gas and quenching rate effect. There was no quenching gas injection in the experiment of Ge and Li content effect, the Ar/O₂ molar ratio was 57.5:2.5. The experiment conditions were summarized in **Table 3.1**.

3.1.2 Analysis Method

The phase identification of synthesized nanoparticles was conducted through X-ray diffraction (XRD, Rigaku Multiflex), operating with a Cu K α source ($\lambda = 0.1541$ nm). The scan mode was set at a speed of 1°/min in the region 10°-90°. The structure of the amorphous part was understood through Raman spectrometer (Raman, LabRAM ARAMIS). The wavelength of laser source in this research was 532 nm. The morphology of products was characterized through transmission electron microscopy (TEM, JEOL JEM-2100HCKM) with an accelerating voltage of 200 kV. Two software, *JADE* 6.5 (Material Data, USA) and *FactSage* 7.2 (Centre for Research in

Computational Thermochemistry, Canada; GTT-Technology, Germany), were used to investigate the amorphous degree and thermodynamic composition during plasma process.

3.2 Experiment results

3.2.1 Effect of Germanium content in Raw Material

The morphology of nanoparticles synthesized by different Ge contents was understood through TEM. The TEM images with electron diffraction are shown in **Fig. 3.2 (a)-(d)**. The focus of electron beam in products is depicted as the red square. The halo in electron diffraction image represents amorphous structure and the unregular diffraction spots indicate low crystallinity. These images indicate the products exist as agglomerated states insides of isolated spherical particles. The diameter of nanoparticles is around 40-50 nm indexed by orange circle.

Temperature influences the morphology of the products during the particle growth process [5]. Particle coalescence is more rapid than coagulation at high temperature. This phenomenon allows spherical particle formation. Coagulation becomes obvious gradually compared to coalescence with temperature decrease. This is because there is no sufficient energy to achieve particle boundary elimination. Agglomerates are formed at low temperature due to coagulation being dominant [6]. The temperature of particle growth in Li-Ge-O system is lower than 1700 K. The reaction temperature region was estimated by thermodynamic equilibrium and the result is shown in section 3.3.1. Thereby, agglomerates instead of spherical particles are formed in Li-Ge-O system.

Figure 3.3 is the XRD spectra for products synthesized by different Ge contents. The low temperature phase Li₄GeO₄ (α -Li₄GeO₄) and high temperature phase Li₄GeO₄(γ -Li₄GeO₄) are the main products in the crystal part. Peaks belonging to Li₂GeO₃ are also detected as the by-product. There is a phase transition from γ -Li₄GeO₄ to α -Li₄GeO₄ around 1006 K [7]. The rapid quenching rate of induction thermal plasma prevents the phase transition, allowing the γ -Li₄GeO₄ to remain in products. Peak intensity of γ -Li₄GeO₄ becomes stronger with Ge molar content increase. This tendency results from the enlarged O-Ge-O angle distribution in high Ge cases and will be discussed in the section 3.3.2.

The estimated amorphous Li₄GeO₄ degree for different Li/Ge molar ratios is shown in **Fig. 3.4**. This result is estimated by *JADE* 6.5 according to XRD spectra using **Eqs. (2.1)** - (2.2). Classification of crystalline and broad amorphous peaks is important based on **Eq. (2.1)**. There are no obvious and sharp peaks in XRD spectrum for amorphous compounds, instead, the broad amorphous peak emerges. Different compounds own different 20 for their amorphous peaks [8]. Amorphous peaks for amorphous Li₄GeO₄ and Li₂GeO₃ are located around 22 and 30 degree, respectively [9,10]. The amorphous Li₄GeO₄ degree is obtained by only estimating the amorphous peak at 22 degree. The estimated amorphous degree rises from 23% to 39% with the molar ratio of Li/Ge rising from 4:1 to 4:1.5. This increase demonstrates Ge promotes amorphous Li₄GeO₄ generation.

Tetrahedron [GeO₄] is the fundamental structure unit for lithium germanate glass, the schematic diagram is shown in **Fig. 3.5 (a)**. The network of amorphous lithium germanate is built by [GeO₄], lithium ions locate in the hole of the network. The strong Ge-O bond is beneficial to resist the destruction of network caused by the Li₂O addition. The topological disorder structure is preserved by the rapid quenching rate, further achieving the amorphous structure in lithium germanate. The Q^n species distribution reflects structure of lithium germanate glass [11,12]. The *n* represents the bridge oxygen (BOs) number connected with tetrahedron [GeO₄]. The schematic diagram of Q^n is presented in **Fig. 3.5 (b)**. Raman spectrum analysis was conducted to investigate Q^n distribution for products.

The Raman spectra are presented in Fig. 3.6 (a)-(c). The gray dots line and blue line represent

the experimental spectrum and cumulative fitting, respectively. The characteristic peaks are fitted by Gaussian function. There are five typical peaks are identified, indicating products consist of five germanate units. Peaks are marked as orange dots line located around 500-600 cm⁻¹ and 730-760 cm⁻¹ are belonged to GeO₄⁴⁻ with bending and stretching vibration, respectively [13]. Peak around 800-810 cm⁻¹ is indexed to isolated GeO₃²⁻ in purple dots line [14]. The Q², tetrahedral [GeO₄] with 2 BOs, species peak around 770-780 cm⁻¹ with green dots line. Two types of Q³ species are observed to exist in lithium germanate glass, they are Q³² (tetrahedral [GeO₄] with 3 BOs connected with Q²) and Q³³ species (tetrahedral [GeO₄] with 3 BOs connected with same Q³), respectively [15,16]. The Q³² and Q³³ species peaks are located around 830-850 cm⁻¹ and 850-880 cm⁻¹ marked pink dots line [15].

Figure 3.7 displays the relative amount of each germanate unit in products synthesized by Ge contents. The relative amounts of each unit can be estimated based on the assumption that the total number of Raman scattering gives rise to the area under the peaks [17]. Estimated result demonstrates that isolated GeO_4^4 percentage occupies the highest point in Li/Ge of 4:1 around 49%, then decreases with Ge molar content increasing because a higher amorphous degree is achieved. Increased Ge molar content results in more Li₂GeO₃ synthesized due to the higher Ge molar amount. The percentage of Q² specie is lower than Q³ in synthesized nanoparticles. Since "germanate anomaly" in lithium germanate glass, the Qⁿ specie distribution is different with lithium silicate glass [16]. The Q² percentage reaches the maximum of around 20 % of total Qⁿ at 10 mol% lithium content, then declines with lithium increase. The Q³ percentage experiences the same increase tendency as the Q² percentage with Li content increasing to 10 mol%. A continuous enhancement is observed in Q³ percentage displays an opposite tendency. Therefore, lithium germanate glass with high Li content (Li≥10 mol%) shows a higher value of Q³ percentage [18].

The above results demonstrate that Ge as the glass former in lithium germanate glass has a positive effect both on amorphous Li_4GeO_4 and high temperature phase Li_4GeO_4 generation. This phenomenon is influenced by topology of tetrahedron [GeO₄] and the reason will be discussed in the section 3.3.2 and 3.3.3.

3.2.2 Effect of Quenching Gas

Quenching rate effect is also studied due to the enhanced quenching rate having a positive effect on amorphous nanoparticles synthesis [19]. Figure 3.8 (a)-(d) displays the TEM images with electron diffraction of nanoparticles synthesized by different quenching gas flow rates. The red square is the focus of the electron beam on product. The halo in electron diffraction image demonstrates amorphous structure. The agglomerated state is also observed in products. The particles indexed by the orange circle show the diameter of 20-30 nm, indicating that quenching gas utilization allows tinier particle generation. This is because quenching gas injection decreases temperature obviously, and more nuclei are generated. The vapor consumption of each nucleus would be declined because the total amount of vapor is constant. Thus, the smaller nanoparticles are obtained with quenching gas injection.

The XRD spectra of the products synthesized by different quenching gas flow rates are shown in **Fig. 3.9**. The main product is crystalline α -Li₄GeO₄ in the case without quenching gas. Crystal peak intensity decreases with quenching gas flow rate increasing to 10 L/min, simultaneously, the α -Li₄GeO₄ peaks disappear. Only the γ -Li₄GeO₄ peaks are observed due to the enhanced quenching rate. The Li₂CO₃ peaks are detected as another by-product besides Li₂GeO₃. The raw material would be totally evaporated and decomposed in high temperature region, and the vapor reactions occur. The C vapor would be reacted with O vapor to form CO₂ and CO vapor above 4000 K based on thermodynamic equilibrium composition in section 3.3.1. The Gibbs energy change of Li_2CO_3 , CO and CO₂ synthesis is shown in **Fig. 3.10**, indicating the Gibbs energy change of CO₂ and CO synthesis is negative and is much lower than Li_2CO_3 above 4000 K. The CO₂ and CO are synthesized preferentially contrasted to Li_2CO_3 at high temperature. These synthesized CO₂ and CO vapor exhaust from system by the vacuum pump as soon as they generate. The lithium germanante nanoparticles are synthesized under 1700 K based on the formation mechanism. Namely, the CO₂ cannot take part in the reaction and Li_2CO_3 would not be synthesized during plasma process. Since the enhanced quenching rate impairs Li_2O condensation and accelerates Li_2O solidification, the unreacted Li_2O would be reserved in products. These Li_2CO_3 are synthesized by unreacted Li_2O with H₂O and CO₂ in atmosphere after plasma process during collection.

Main product gradually changes to Li₂GeO₃ in crystal part with the quenching gas flow rate continuously increasing to 20 L/min. This situation is associated with the supersaturation ratio for each compound in Li-Ge-O system, more details will be discussed in section 3.3.1 after formation mechanism investigation.

Figure 3.11 presents the estimated amorphous Li₄GeO₄ degree of product synthesized by different quenching gas flow rates. Amorphous Li₄GeO₄ degree increases to around 65% after 10 L/min quenching gas injection. However, this value declines to around 57% and 36 % with quenching gas flow rates increasing to 15 L/min and 20 L/min, respectively. This situation relates to the composition of the final product, the enhanced quenching rate impairs Li₄GeO₄ synthesis. The less total amount of Li₄GeO₄ in 15 L/min and 20 L/min cases results in the relative amount of amorphous Li₄GeO₄ also experiencing a decrease. Thus, the maximum of amorphous Li₄GeO₄ is achieved in the 10 L/min case. More details will be discussed in section 3.3.1 after the formation mechanism.

The products synthesized by different quenching gas flow rates consist of GeO4⁴⁻, GeO3²⁻, Q²,

and Q^3 based on Raman analysis. Figure 3.12 shows the quantified result of Raman spectra. The GeO₄⁴⁻ percentage shows a declining trend with the rise of quenching gas flow rate. An obvious increase is observed in GeO₃²⁻ from 7% to 18% with flow rate increasing from 0 L/min to 20 L/min. This tendency is consistent with XRD results. The Q³ percentage presents a rise with quenching gas flow rate increase, while the Q² percentage has an opposite tendency. This situation demonstrates fewer non-bridge oxygen NBO bonds in the amorphous part of products at high flow rate of quenching gas. Since the enhanced quenching rate impairs Li₂O dominant condensation, meaning less Li₂O participates in reactions and more BO bonds are preserved in high flow rate cases. The relationship between quenching gas flow rate and condensation rate will discuss in the section 3.3.1.

The above results reveal quenching gas injection benefits amorphous Li₄GeO₄ generation and high temperature phase preservation. However, the excessive quenching gas flow rate prevents Li₄GeO₄ generation.

3.2.3 Effect of Carrier Gas

Rapid quenching rate is a significant factor for amorphous nanoparticle synthesis. Besides counter-flow quenching gas injection and addition of O₂ into sheath gas, enhancement of carrier gas flow rate also allows particles to pass through plasma faster. Namely, high carrier gas flow rate reduces the particle residence time and accelerates particle solidification. Thus, the effect of carrier gas flow rate was investigated. The raw material was injected into plasma by 3 L/min, 4.5 L/min and 6 L/min Ar carrier gas, the feeding rate was fixed at 300 mg/min. The Li/Ge molar ratio in raw material was 4:1, no quenching gas injection during plasma process.

Figure 3.13 displays the XRD spectra of nanoparticles synthesized by different carrier gas flow rates. The spectra demonstrate that no α -Li₄GeO₄ synthesized in 4.5 and 6 L/min cases rather than

 γ -Li₄GeO₄ peaks are observed in crystalline part. Meanwhile, the Li₂GeO₃ peaks gradually become dominant with carrier gas flow rate increase. The amorphous peak is observed obviously in 4.5 and 6 L/min cases, meaning more amorphous nanoparticles are obtained in high flow rate cases. The estimated amorphous Li₄GeO₄ degree is presented in **Fig. 3.14**, indicating the amorphous degree increases to 54% in 6 L/min case. The enhanced flow rate of carrier gas leads to the particles passing through the high temperature region more rapidly, which reduces the duration time of liquid state and prevents the structure transformation from disorder to order. Hence, the enhanced flow rates benefit amorphous nanoparticles synthesized due to shortening residence time.

The Raman spectra indicate four germanate structure units GeO_4^{4-} , GeO_3^{2-} , Q^2 , and Q^{33} and Q^{32} , in products. **Figure 3.15** is the results of qualified Raman spectra, indicating the percentage of GeO_4^{4-} and Q^2 experience a downward tendency with flow rate increase. This is because less Li₂O takes part in the reaction and more BOs are preserved. In addition, the Li₂GeO₃ percentage presents an increase, resulting from the promoted GeO dominant condensation which is achieved in high flow rate cases. More details will be discussed in section 3.3.1.

Above results reveal that the short duration time in thermal plasma benefits amorphous and high temperature phase Li₄GeO₄ synthesized, while also resulting in the by-product Li₂GeO₃ being synthesized.

3.2.4 Effect of Lithium Content in Raw Material

The above experiment results present that Li_2GeO_3 with a Li/Ge molar ratio of 2 exists in products, while the Li/Ge molar ratio is 4 in raw material. Lithium loss occurs during the plasma process. Hence, the experiment on excess Li in raw material was conducted. The Li/Ge molar ratio was 4:1, 4.25:1, and 4.5:1, respectively. The raw material was injected into plasma at 300

mg/min. There was no quenching gas utilization during plasma process.

Figure 3.16 shows the XRD spectra of nanoparticles synthesized by different Li contents. The main product in crystal part is Li₂GeO₃, the Li₄GeO₄ exists as high temperature phase γ -Li₄GeO₄. In addition, another by-product Li₂CO₃ is observed. By-product Li₂CO₃ is considered synthesized by CO₂ in the atmosphere and unreacted Li₂O during collection time according to section 3.2.2 discussion. The detection of Li₂CO₃ means there is still some Li₂O not taking part in reaction during plasma process.

The increased Li content in raw material allows Li₂O to achieve supersaturation earlier. The Li-rich Li₄GeO₄ is mainly synthesized at the early stage of condensation, the earlier achievement of supersaturation leads to Li₄GeO₄ being synthesized at the higher temperature position. The synthesized and unstable Li₄GeO₄ would decompose into Li₂O, GeO and O₂ due to the high temperature, these decomposed Li₂O and GeO flow to the downstream region. Because the solidification temperature of Li₂O is higher than that of GeO, the Li₂O would earlier solidify at the downstream region than GeO. This phenomenon impairs the Li₂O participation of reaction and results in more GeO-rich Li₂GeO₃ being synthesized. The amorphous Li₄GeO₄ degree of products synthesized by different Li content is displayed in **Fig 3.17**, indicating there is no obvious discrepancy in three cases although the amorphous peak can be clearly observed in high Li content cases.

The Q^n species distribution was estimated based on Raman spectra and shown in **Fig. 3.18**. The percentage of GeO_3^{2-} experiences an upward tendency while GeO_4^{4-} has an opposite trend, corresponding to XRD results.

3.2.5 Effect of Oxygen Flow Rate

Addition of diatomic O₂ into monoatomic Ar sheath gas can shrink plasma flow, this situation

prefers amorphous structure synthesis based on Chapter 2 results. Here, the O_2 flow rate effect was also studied. The value of molar ratio is shown in **Table. 3.1**. The Li/Ge molar ratio of raw material was 4:1, there is no quenching gas injection during the plasma process.

Figure 3.19 is the XRD spectra of nanoparticles synthesized by different O_2 flow rates. The main product of three conditions is α -Li₄GeO₄, the peak intensity of γ -Li₄GeO₄ and Li₂GeO₃ becomes obvious with O_2 flow rates increase. Plasma flow is shrunk by adding diatomic gas O_2 into Ar, the steeper temperature gradient is obtained due to the higher thermal conductivity of O_2 . This phenomenon contributes to high temperature phase γ -Li₄GeO₄ being preserved. Meanwhile, the steeper temperature gradient allows following-stage condensation to be advanced and promotes GeO condensation. Increased Li₂GeO₃ is acquired at high O₂ flow rate cases.

Figure 3.20 displays the amorphous Li_4GeO_4 degree of nanoparticles synthesized by different O_2 flow rates. Since the steeper temperature gradient caused by O_2 addition, an increase tendency is observed in amorphous Li_4GeO_4 degree with O_2 flow rate rising. This result also indicates three conditions have low amorphous degree, the 5 L/min case occupies the highest amorphous degree of 25%.

3.3. Discussion

3.3.1 Formation Mechanism of Lithium Germanate Nanoparticles

The formation mechanism of amorphous nanoparticles synthesized by induction thermal plasma is investigated in order to understand the experiment results deeply and theoretically. Since the unique superiority of induction thermal plasma, the formation mechanism of this advanced fabrication method is different from the conventional method [6].

The raw materials evaporate and decompose immediately in high temperature region after injecting into thermal plasma. Atoms collide with each other to form small clusters (embryos) containing a few molecules by vapor phase reactions or just by coalescence. Actually, most of these small clusters would disappear in a short time because most of them are thermodynamically unstable. Simultaneously, these small clusters are transported to lower temperature region. Vapor saturation pressure declines due to temperature decrease, the partial vapor pressure exceeds saturation pressure to reach supersaturation. Nuclei are generated under the size of embryos achieve critical crystal size and the vapor satisfies supersaturate. This supersaturation vapor is identified as the nucleation phase. Particles grow continuously by heterogeneous co-condensation which starts as soon as nucleus generation in plasma. Condensation phase is considered as the vapor participating in condensation except for nucleation vapor. Nucleation phase and condensation phase co-condense on the surface of nuclei and mix well in the liquid state before solidification. Various reactions occur to form different compounds during the condensation process. Subsequently, coagulation starts after compound particle solidification starts by colliding with each other randomly. Finally, nanoparticles are synthesized after nucleation, and coagulation [20,21].

Clarification of the nucleation and condensation phase during the plasma process is necessary according to above nanoparticle generation process. The nucleation temperature of each substance in Li-Ge-O system is investigated based on Eqs. (2.3) - (2.6).

The nucleation temperatures for Li and Ge are 974 K and 2155 K under 300 mg/min feeding rate, respectively. Because the physical properties of oxides are limited and nucleation temperature is similar to melting point [22]. The melting point is regarded as the nucleation temperature for oxides in this study. **Figure 3.21** presents the nucleation temperature of the Li, Ge and the boiling point, melting point of oxides in Li-Ge-O system. Melting point and boiling point are obtained from Lang's Handbook of Chemistry [23]. **Figure 3.21** demonstrates that Ge occupies the highest nucleation temperature and should nucleate first in Li-Ge-O system.

The homogenous nucleation also strongly depends on the saturation ratio besides the nucleation temperature. Thermodynamic equilibrium composition for Li-Ge-O system from 1000 K to 5000 K is investigated aiming to understand the partial vapor pressure of different species around their nucleation temperature. The nuclei cannot stably exist at high temperature because the high temperature would result in generated nuclei decomposing. The nucleation phase and condensation phase would be solidified below 1000 K in Li-Ge-O system. The thermodynamic equilibrium composition is estimated with a temperature range of 1000-5000 K. The estimated result is shown in **Fig. 3.22**. This result was developed by *FactSage* 7.2 with following conditions. Raw material feeding rate is fixed at 300 mg/min. Sheath gas flow rates for Ar and O₂ are 57.5 L/min, and 2.5 L/min, respectively. The nuclei cannot stably exist at high temperature because the high temperature would result in generated nuclei decomposing. The nucleation phase and condensation phase would be solidified below 1000 K in Li-Ge-O system. The thermodynamic equilibrium composition is estimated with a temperature range of 1000-5000 K. The estimated the high temperature would result in generated nuclei decomposing. The nucleation phase and condensation phase would be solidified below 1000 K in Li-Ge-O system. The thermodynamic equilibrium composition is estimated with a temperature range of 1000-5000 K, the ion content is very low in this temperature region. Thus, the ion effect can be negligible.

This result demonstrates that Ge vapor is consumed by the reaction with O vapor to form into GeO vapor below 4000 K. Partial vapor pressure of Ge is too low to support Ge nucleation around 2155 K. Germanium is not the nucleation phase in Li-Ge-O system. Meanwhile, there is an obvious deviation in the Li₂O boiling point. This is because Li mainly exists as Li vapor and LiO vapor at high temperature, the Li₂O cannot achieve saturation state caused by the low partial vapor pressure. The Li₂O nucleates around 1700 K following Ge according to **Fig. 3.21**. Moreover, the vapor pressure of Li₂O is also sufficient to satisfy supersaturation around its nucleation temperature. Therefore, the nucleation phase can be identified as Li₂O in Li-Ge-O system.

The formation mechanism is put forward based on thermodynamic analysis and experiment results. The process is shown in **Fig. 3.23**. The mixture of GeO₂ and Li₂CO₃ decomposes

completely in high temperature region, then particles react with each other in vapor phase. The GeO and Li₂O vapor are synthesized during this period. Continuously produced Li₂O vapors flow to downstream with lower temperature. Homogeneous nucleation starts when the saturation ratio of Li₂O achieves unity. Vapor of GeO and Li₂O start to heterogeneously co-condense on Li₂O nucleus subsequently. The Li-Ge-O particles are generated in this period.

Condensation is driven by the saturation ratio during the plasma process [24]. The Li₂O-rich particles Li₄GeO₄ are synthesized at early stage of condensation ascribing to a higher saturation ratio of Li₂O than GeO. **Equation (3.1)** is the dominant reaction at the early stage. The dominant reaction is replaced gradually by **Eq. (3.2)** with Li₂O vapor consumption and GeO vapor starts to achieve supersaturation. The GeO-rich particles Li₂GeO₃ are synthesized mainly at the following stage. The synthesized Li₄GeO₄ and Li₂GeO₃ particles grow continuously by coagulation after solidification starts. Finally, particles reach filter and wall of inner chamber.

GeO (g)+2Li₂O (l)+
$$\frac{1}{2}O_2(g) \rightarrow Li_4GeO_4(s)$$
 (3.1)

GeO (g)+Li₂O (l)+
$$\frac{1}{2}$$
O₂(g)→Li₂GeO₃(s) (3.2)

The rapid quenching rate impedes the order growth of particles during plasma process [25]. Amorphous structure is achieved due to the chaotic structure being preserved. This impedance can be intensified by high quenching rate. Thus, enhanced amorphous degree is achieved after quenching gas injection.

The formation mechanism can explain the composition variation of products synthesized by different quenching gas and carrier gas flow rates. The synthesis of Ge-rich Li₂GeO₃ is mainly driven by GeO dominant condensation at the following condensation stage based on the formation mechanism. Promoted GeO condensation results in more Li₂GeO₃ synthesis. The duration of Li₂O

dominant condensation is shortened after quenching gas injection and carrier gas enhancement. Because synthesized particles earlier reach low temperature region due to the sharper temperature gradient caused by enhanced quenching gas and carrier gas flow rate. Saturation ratio of GeO is risen simultaneously ascribing to lower temperature, which allows the GeO dominant condensation to be advanced. These phenomena promote GeO condensation and GeO-rich Li₂GeO₃ generation. The recirculation zone is also suppressed by the quenching gas injection, resulting in the reduction of particle growth time. There is no adequate time for Li₂O to condense on the nucleus. These unreacted Li₂O is transported to low temperature region for solidification, further contacting with H₂O and CO₂ to form Li₂CO₃ during collection time. Hence, the percentage of Li₂GeO₃ rises with the quenching gas and carrier gas flow rate increase, moreover, the Li₂CO₃ is detected as the by-product in high quenching gas flow rate cases. The declined amorphous Li₄GeO₄ degree was observed in 15 L/min and 20 L/min quenching gas cases resulting from the less Li₄GeO₄ synthesis under excessive quenching gas.

3.3.2 Short-range Order in Amorphous Lithium Germanate

The amorphous material shows topological disorder in structure [26,27]. The short-range order (SRO), in the range 2-5 Å, of amorphous lithium germanate is quantified by distribution of intratetrahedral O-Ge-O angle [28]. **Figure 3.24 (a)** shows the illustration of intratetrahedral O-Ge-O angle. The O-Ge-O angle ranges from 80 to 160 degrees at high temperature, while this range shrinks to 90 to 110 degrees at room temperature [29]. The rapid quenching rate allows broad intratetrahedral O-Ge-O angle distribution to be preserved after the plasma process. These chaotic angles increase the disorder of product in SRO, which benefits amorphous structure formation. Enhanced quenching rate facilitates preservation of broad angle distribution. The more chaotic state is obtained in SRO. Therefore, the higher amorphous Li₄GeO₄ degree is acquired

after quenching gas injection.

The intratetrahedron O-Ge-O angular excursion is also enlarged with Ge composition increase. Increased Ge molar amount broadens intratetrahedral O-Ge-O angle distribution in germanate glass [30]. Since the increase of Ge composition inevitably leads to Ge-Ge homopolar bonds occurring, further leading to more small rings generation in amorphous [31,32]. These small rings allow amorphous transforms to stressed rigid phase which occupies the high network connectivity. Asymmetric bending motions in [GeO4] tetrahedron occur as the additional cross-links force to soften interactions in order to adapt and break the corresponding constraint [33]. This phenomenon leads to the broader O-Ge-O angle distribution and higher SRO chaos degree. Increased amorphous Li4GeO4 degree is obtained because more chaotic state is achieved in SRO in high Ge molar amount case. Therefore, an increase tendency in amorphous degree is observed with Ge molar content increase in raw material.

The enhanced intensity of γ -Li₄GeO₄ peaks is also observed with Ge molar content increase, this situation is also associated with the intratetrahedral O-Ge-O angle distribution. The high temperature phase γ -Li₄GeO₄ occupies a wider angular distribution than low temperature phase α -Li₄GeO₄[29]. Thus, enlarged O-Ge-O angle distribution also facilitates γ -Li₄GeO₄ synthesis in high Ge content cases.

3.3.3 Intermediate-range Order in Amorphous Lithium Germanate

Intermediate-range order (IRO) in the range 5-20 Å is another index of topological order to describe the amorphous structure. The intertetrahedral angle Ge-O-Ge distribution represents IRO in amorphous lithium germanate [34]. The illustration is presented in **Fig. 3.24 (b)**. Tetrahedrons [GeO₄] are linked with each other through corner-sharing rather than edge-sharing in amorphous lithium germenate. This phenomenon allows the most conformational flexibility in the relative

rotational orientation among [GeO₄] tetrahedrons, which contributes to amorphous structure formation. The angle distribution of Ge-O-Ge is also affected by temperature. The increasingly broader angular distribution is observed with temperature rise [29]. Transformation of the Ge-O-Ge angle into a constant can be prevented by the fast quenching rate during the plasma process, further achieving the disorder in product and obtaining amorphous nanoparticles.

Enhanced quenching rate benefits the preservation of broader Ge-O-Ge angle distribution. This phenomenon increases the chaotic state in IRO of products. The quenching rate increases from 3.2×10^4 K/s without quenching gas to 1.3×10^5 K/s after 20 L/min quenching gas injection [20]. Thus, the increased amorphous Li₄GeO₄ degree can be achieved after quenching gas injection ascribing to the higher IRO chaos. The quenching gas injection benefits high disorder both in SRO and IRO simultaneously, further achieving the higher amorphous degree of lithium germanate.

3.4. Conclusion

Amorphous Li₄GeO₄ nanoparticles were synthesized by induction thermal plasma successfully first time. The formation mechanism was investigated based on thermodynamic analysis and experiment results. Effect of short-range and intermediate-range order on product composition, structure and amorphous degree is studied.

The chemical discrepancy was presented in lithium germanate nanoparticles synthesized at different stages of heterogeneous condensation. Lithium-rich nanoparticles Li₄GeO₄ are mainly synthesized at early stage of condensation because of more rapid condensation rate of Li₂O than GeO. By-products Li₂GeO₃ are mainly synthesized at the following condensation stage which GeO condensation is dominant. Duration time of Li₂O dominant condensation is pressed by steeper temperature gradient which is caused by counter quenching gas injection. Hence, more

Li₂GeO₃ are synthesized under quenching gas with high flow rate. Angle distribution of intratetrahedral O-Ge-O and intertetrahedral Ge-O-Ge is wider in high temperature. Increased quenching rate prevents the flexible angles transform to the fixed value. The disorder in SRO and IRO is preserved, and an enhanced amorphous degree is achieved, the increased quenching rate contributes to high amorphous degree due to impairment of particles growth in order in long range.

Increased glass former Ge content in raw material benefits amorphous Li₄GeO₄ and high temperature phase γ -Li₄GeO₄ formation. Because more Ge allows intratetrahedral O-Ge-O angle achieves enlarged angular distribution which enhances product disorderly in SRO. Simultaneously, this extended angle distribution which is reserved by rapid quenching rate allows more γ -Li₄GeO₄ remain in products after plasma processing.

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Parameter	Condition
Input power [kW]	20
Pressure [kPa]	101.3
Frequency [MHz]	4
Sheath gas rate [L/min]	60 (Ar+O ₂)
Inner gas rate [L/min]	5 (Ar)
Carrier gas rate [L/min]	3, 4.5, 6 (Ar)
Quenching gas rate [L/min]	0, 10, 20 (Ar)
Feed rate [mg/min]	300
Ar/O ₂ molar ratio [-]	59:1, 57.5:2.5, 55:5
L/Ge molar ratio [-]	4:1, 4:1.25, 4:1.5,
	4.25:1, 4.5:1

 Table 3.1. Experimental conditions for induction thermal plasma system.



Fig. 3.1. Schematic diagram of amorphous Li₄GeO₄ synthesized by induction thermal plasma.



Fig. 3.2. TEM images of products synthesized by (a) 4:1, (b) 4:1.25, (c) 4:1.5 Li/Ge molar ratio. The red square is the focus of the electron beam on product. The corresponding diffraction pattern is shown in (d).


Fig. 3.3. XRD spectra of products synthesized by 4:1, 4:1.25, 4:1.5 Li/Ge molar ratio. Blue round, yellow round, green square represents γ-Li₄GeO₄, α-Li₄GeO₄, and Li₂GeO₃, respectively.



Fig. 3.4 Estimated amorphous Li₄GeO₄ degree of product synthesized by different Li/Ge molar ratios. The error bars represent the standard errors of the corresponding average.



Fig. 3.5. Schematic diagram of (a) [GeO₄] tetrahedron, (b) Q^n species in Li-Ge-O system. The Q^2 , Q^{32} , and Q^{33} is illustrated by blue, green, and orange rectangle, respectively.



Fig. 3.6. Raman spectra of products synthesized by different Ge contents. (a) 4:1, (b) 4:1.25, (c) 4:1.5. Gray dots line is the experimental results, the blue line is the cumulative fitting.



Fig. 3.7. Relative amount of different germanate units of products synthesized by different Ge contents. The error bars represent the standard errors of the corresponding average.



Fig. 3.8. TEM images of products synthesized by (a) 0 L/min, (b) 10 L/min, (c) 20 L/min Ar quenching gas. The red square is the focus of the electron beam on product. The corresponding diffraction pattern is shown in (d).



Fig. 3.9. XRD spectra of products synthesized by different quenching gas flow rates. Blue round, yellow round, green square and pink triangle represents γ-Li₄GeO₄, α-Li₄GeO₄, Li₂GeO₃ and Li₂CO₃, respectively.



Fig. 3.10. Gibbs energy change of Li₂CO₃, CO₂ and CO with temperature region of 1000-5000 K.



Fig. 3.11. Estimated amorphous Li₄GeO₄ degree of product synthesized by different quenching gas flow rates. The error bars represent the standard errors of the corresponding average.



Fig. 3.12. Relative amount of different germanate units of products synthesized by different quenching gas flow rates. The error bar represents the standard errors of the corresponding average.



Fig. 3.13. XRD spectra of products synthesized by different carrier gas flow rates. Blue round, yellow round, and green square represents γ -Li₄GeO₄, α -Li₄GeO₄, and Li₂GeO₃, respectively.



Fig. 3.14. Estimated amorphous Li₄GeO₄ degree of product synthesized by different carrier gas flow rates. The error bars represent the standard errors of the corresponding average.



Fig. 3.15. Relative amount of different germanate units of products synthesized by different carrier gas flow rates. The error bar represents the standard errors of the corresponding average.



Fig. 3.16. XRD spectra of products synthesized by 4:1, 4.25:1, 4.5:1 Li/Ge molar ratio. Blue round, yellow round, green square and pink triangle represents γ-Li₄GeO₄, α-Li₄GeO₄, Li₂GeO₃, and Li₂CO₃, respectively.



Fig. 3.17. Estimated amorphous Li₄GeO₄ degree of product synthesized by different Li contents. The error bars represent the standard errors of the corresponding average.



Fig. 3.18. Relative amount of different germanate units of products synthesized by different Li contents. The error bar represents the standard errors of the corresponding average.



Fig. 3.19. XRD spectra of products synthesized by different O₂ flow rates. Blue round, yellow round, and green square represents γ -Li₄GeO₄, α -Li₄GeO₄, and Li₂GeO₃, respectively.



Fig. 3.20. Estimated amorphous Li₄GeO₄ degree of product synthesized by different O₂ flow rates. The error bars represent the standard errors of the corresponding average.



Fig. 3.21. The melting, boiling, and nucleation temperature of Ge, Li, and oxides.



Fig. 3.22. Thermal equilibrium of the Li-Ge-O system. Feeding rate is 300 mg/min with Li/Ge molar ratio 4/1, Ar/O₂ is 57.5/2.5.



Fig. 3.23. Formation mechanism of Li-Ge-O nanoparticles by induction thermal plasma.



Fig. 3.24. Illustrations of short-range order and intermediate-range order in Li₄GeO₄. (a). Short-range order is defined in terms of 4-coordination tetrahedron and θ is the O-Ge-O angle; (b). Intermediate-range order is defined in terms of the connection of tetrahedrons and φ is the Ge-O-Ge angle.

4. Synthesis of Amorphous Li₅AlO₄ Nanoparticles

Amorphous Li_5AIO_4 has a high ion conductivity and low electron conductivity at room temperature, these advantages satisfy the solid electrolyte requirements [1,2]. The high O/Al value of Li_5AIO_4 allows Al to function as the network former, although Al is a typical glass intermediate instead of the former. [3,4]. In addition, decreasing particle size to the nanoscale can provide a larger connection area between electrode and electrolyte. [5]. Hence, amorphous Li_5AIO_4 nanoparticles were selected as a target material.

This chapter focuses on the synthesis of amorphous Li₅AlO₄ nanoparticles by induction thermal plasma with different Ar quenching gas flow rates and Li/Al molar ratios. The Li content effect, quenching rate effect and formation mechanism were investigated based on thermodynamic analysis and experiment results.

4.1. Experiment

4.1.1 Experiment Configuration and Procedure

The experiment device consists of power supply, powder feeder, plasma torch, reaction chamber cooled by water, quenching tube and product

ion filter, the schematic illustration is shown in **Fig. 4.1**. Quench tube was placed 15 cm below plasma torch. Quenching gas was injected from bottom to offer a sharper temperature gradient. The mixture of Ar and O_2 with a molar ratio 57.5:2.5 was used as sheath gas with a total flow rate of 60 L/min. Raw material with feeding rate of 300 mg/min was injected into plasma by Ar. The experiment conditions are summarized in **Table. 4.1**.

Raw material consists of Li_2CO_3 (purity 99%, Honjo Chemical Corporation) and α -Al₂O₃ (purity 99.9%, Kojundo Chemical Laboratory). No quenching gas injection in different Li/Al molar ratios experiments. The Li/Al molar ratio was fixed at 5:1 in different quenching rates experiments.

4.1.2 Analysis Method

The phase identification of prepared nanoparticles was detected by X-ray diffraction (XRD, Rigaku Multifle) with a Cu K α source ($\lambda = 0.1541$ nm). The continue scan was conducted in a 20 range of 10°-90° at a scan speed of 1°/min. Aluminate unit structure was investigated by Raman spectrometer (Raman, LabRAM ARAMIS), the laser source wavelength fixed at 532 nm. The morphology of prepared nanoparticles was observed by transmission electron microscopy with an accelerating voltage of 200 kV (TEM, JEOL JEM-2100HCKM). There were three software, *JAED* 6.5 (Material Data, USA), *Image J* (National Institutes of Health, USA), and *Factsage* 7.2 (Centre for Research in Computational Thermochemistry, Canada; GTT-Technology, Germany) were used to estimate amorphous degree, diameter distribution of products and thermodynamic composition during plasma process, respectively.

4.2. Experiment Results

4.2.1 Effect of Quenching Gas

Figure 4.2 shows the TEM images and diffraction pattern images of nanoparticles synthesized by different quenching gas flow rates. The focus of electron beam in product is depicted as red square in **Fig. 4.2 (c)**, corresponding diffraction pattern image is shown in **Fig. 4.2 (d)**. There are no regular diffraction spots and rings in **Fig. 4.2 (d)**, indicating the product exists as amorphous structure. The nanoparticles synthesized without quenching gas present spherical morphology which is indexed by the orange circle in **Fig. 4.2 (a)**. Diameter distribution was estimated by *Image J*. More than 200 different particles were countered to obtain results based on TEM images, the estimated result is presented in **Fig. 4.3**. The diameter of nanoparticles ranges from several nanometers to tens of nanometers with an average diameter of 15 nm.

Agglomerates rather than isolated spherical particles are observed in the 10 L/min and 20 L/min quenching gas cases. Spherical particles are produced at high temperature due to coalescence-dominant, while agglomerate occurs at low temperature caused by the dominant coagulation [6,7]. The temperature gradient is sharpened by quenching gas injection, and results in particles growing at lower temperature. Thus, agglomerates are observed in the quenching gas case.

Phase identification of products was investigated by XRD, and the XRD spectra are shown in **Fig. 4.4**. The Li₂CO₃ and high temperature phase LiAlO₂ (γ -LiAlO₂) are detected as by-products in crystalline parts, meanwhile, amorphous peak emerges in XRD spectra. The phase transition can be prevented by the rapid quenching rate of thermal plasma, the γ -LiAlO₂ is preserved in products. Since the total decomposition of raw material, the C vapor reacts with O vapor to form CO₂ and CO vapor before nucleation. The thermodynamic equilibrium composition result is presented in section 4.3.1. Synthesized CO₂ vapor exhaust from the system by vacuum pump, and does not participate in nanoparticle synthesis process [8]. The Li₂CO₃ is considered synthesized by CO₂ in atmosphere with unreacted lithium or lithium oxide after plasma process [9]. The crystal peak intensity becomes weak with quenching gas increase, simultaneously, amorphous peak becomes obvious. The XRD spectra indicate that more amorphous nanoparticles were obtained at high quenching gas flow rate.

The amorphous degree of product is estimated by *JADE* 6.5 based on XRD spectra using **Eqs.** (2.1) - (2.2). The black line in **Figure 4.5** is the estimated amorphous degree of products synthesized by different quenching gas flow rates. The amorphous degree is around 50% without quenching gas injection, increasing to around 82% and 90% after 10 L/min and 20 L/min quenching gas injection, respectively.

The aluminate units and connectivity of these units play significant roles in the amorphous structure [10]. Octahedron [AlO₆] and tetrahedron [AlO₄] are the two main structure units for lithium aluminate, corresponding illustration is shown in **Fig. 4.6**. The Li₅AlO₄ is built by [AlO₄] tetrahedrons [11,12]. Transformation from [AlO₆] to [AlO₄] is influenced by temperature distribution and O/Al molar ratio [13]. Raman spectrometer was conducted in order to understand the unit structure and distribution in products, further understand the effect of different experiment conditions.

Figure 4.7 (a) - (c) are the Raman spectra of products synthesized by different quenching gas flow rates. Gray dots line and blue line represent experiment spectrum and cumulative fitting, respectively. There are six characteristic peaks identified after fitting by Gaussian function in products. The peak located around 480-500 cm⁻¹ belongs to AlO_2^{-} [14]. Peaks sited to around 500-

520 cm⁻¹, 600 cm⁻¹, and 730-800 cm⁻¹ are indexed to [AlO₄] with bridge oxygens (BOs), [AlO₆] and [AlO₄] with non-bridge oxygens (NBOs), respectively [15,16]. The CO_3^{2-} peak is placed around 1100 cm⁻¹ [17]. Because no peaks belonged to [AlO₆] in XRD spectra, meanwhile, the [AlO₆] is also detected in lithium aluminate glass [16,18]. The [AlO₆] is considered to exist as amorphous in this experiment.

Figure 4.8 is the estimated relative amounts of different units for products synthesized by different quenching gas flow rates. This result is obtained based on the following assumption. The total number of Raman scattering gives rise to the area under the peaks, each Gaussian peak area should be related to the amount of corresponding structural unit [19,20]. The estimated result demonstrates that the by-products Li₂CO₃ and γ -LiAlO₂ decrease obviously after quenching gas injection. Percentage of CO₃²⁻ and AlO₂⁻ continually decrease to around 16% and 10% with flow rate increase to 20 L/min, respectively. Simultaneously, the percentage of [AlO₄] with BOs also reduces to 23% in 20 L/min case. An opposite tendency is observed in the percentage of [AlO₆] to [AlO₄] is impaired by quenching gas and fewer BO bonds exist in products. Above phenomena are related to condensation rate of different species during plasma process. The enhanced quenching gas flow rate allows more Li₂O to take part in reactions, the BO bonds are destroyed by these increased Li₂O and more NBOs are formed. The transformation time from [AlO₆] to [AlO₄] is shortened by enhanced quenching rate, and more [AlO₆] are detected in products. Details will be discussed in the section 4.3.2.

The estimated amorphous Li₅AlO₄ degree can be obtained after understanding the relative amount of each unit. Four compounds are known in Li-Al-O system: LiAl₅O₈, Li₂Al₄O₇, LiAlO₂, and Li₅AlO₄ [21]. The first two compounds contain [AlO₆] octahedrons, while the aluminate unit of the latter two is only [AlO₄] tetrahedron [21]. Network supported by tetrahedrons more easily forms amorphous structure compared to octahedrons according to Zachariasen's rule [10]. Thus, the LiAl₅O₈ and Li₂Al₄O₇ prefer to form crystalline, while LiAlO₂ and Li₅AlO₄ prefer to form amorphous at the same quenching rate. The higher coordination number of Al results in harder amorphous formation [22]. The LiAlO₂ melt possesses higher Al coordination number compared to Li₅AlO₄, indicating Li₅AlO₄ more easily acquires amorphous structure than LiAlO₂ [22]. Thus, all Li₅AlO₄ exists as amorphous while part of LiAlO₂ exists as amorphous.

The XRD spectra indicate that only γ -LiAlO₂ peaks are detected for lithium aluminate in crystal part, that is, no LiAl₅O₈ and Li₂Al₄O₇ are synthesized during the plasma process. Composition of products can be identified based on above description. Amorphous part contains Li₅AlO₄ and parts of LiAlO₂, crystalline part contains Li₂CO₃ and parts of LiAlO₂. Amorphous Li₅AlO₄ degree is estimated according to following equations:

$$W_{a}(\text{Li}_{5}\text{AlO}_{4}) = W_{amorphous} - W_{a}(\text{LiAlO}_{2})$$
(4.1)

$$W_{a}(\text{LiAlO}_{2}) = W(\text{LiAlO}_{2}) - [DOC - W(\text{Li}_{2}\text{CO}_{3})]$$

$$(4.2)$$

where W_a (Li₅AlO₄) and W_a (LiAlO₂) represent relative amount of amorphous Li₅AlO₄ and LiAlO₂, respectively. W (LiAlO₂) and W (Li₂CO₃) refer to relative amounts of LiAlO₂ and Li₂CO₃. The red line in **Fig. 4.5** shows the estimated amorphous Li₅AlO₄ degree of products synthesized by different quenching gas flow rates. Enhanced amorphous Li₅AlO₄ degree is achieved in high quenching rate condition, the value increases to around 82% at 20 L/min of quenching gas.

The above results indicate that high quenching rate benefits amorphous Li₅AlO₄ synthesis at Li/Al molar ratio 5:1. Meanwhile, the high quenching rate attributes to by-product reduction. The reason for this phenomenon is related to saturation ratio of different vapor phases, more details will be discussed in next section.

4.2.2 Effect of Li Content in Raw Material

The spherical particles are observed in products synthesized by different Li/Al molar ratios, the TEM images are shown in **Fig. 4.9**. The nanoparticles indexed by orange circles display a diameter of around 20 nm. Some particles indexed by blue square even have a very tiny diameter blew than 10 nm. Since the nucleation temperature is around 3000 K in Li-Al-O system, which allows the particles can grow in high temperature region. The nucleation temperature is discussed on the section 4.3.1. The coalescence among particles is more dominant than coagulate as previously discussed, leading to the formation of spherical particles.

The main products in the crystal part were identified as Li₂CO₃ and γ-LiAlO₂ according to the

XRD spectra, and the XRD spectra are shown in **Fig. 4.10**. Peak intensity of Li_2CO_3 and γ -LiAlO₂ becomes weaker with the Li/Al molar ratio value increasing, which reveals more amorphous were synthesized after Li/Al molar ratio rising. Amorphous degree of products was estimated based on **Eqs. (2.1) - (2.2)**, and the estimated results are presented in **Fig. 4.11**. The result indicates that the enhanced amorphous degree of products was obtained by the high Li content in raw material.

Aluminate unit distribution in products was also investigated by Raman spectrometer. Same characteristic peaks were detected in quenching rate effect experiments, the product consists of AlO_2^- , $[AlO_4]$ with BOs, $[AlO_6]$, $[AlO_4]$ with NBOs, and $CO_3^{2^-}$. Figure 4.12 is the relative amounts of different units in products. Percentage of AlO_2^- , $CO_3^{2^-}$, and $[AlO_4]$ with BOs show a downtrend, while the percentage of $[AlO_6]$ and $[AlO_4]$ with NBOs have an opposite tendency. Estimated amorphous Li_5AlO_4 degree is presented in Fig. 4.11 as the red line. Amorphous Li_5AlO_4 degree enhances to around 61% in Li/Al molar ratio of 5.75 indicating that amorphous Li_5AlO_4 nanoparticles prefer to synthesize in a condition that Li molar amount excesses of its stoichiometric ratio.

The above results demonstrate that excessive Li content in raw material promotes amorphous Li₅AlO₄ nanoparticles synthesis, simultaneously, preventing by-product generation. Details will be discussed in the next section.

4.3. Discussion

4.3.1 Formation Mechanism of Lithium Aluminate Nanoparticles

The structure and the chemical composition of products are closely related to chemical reactions and particle growth during plasma process. Investigation of formation mechanism is a powerful method to understand experiment condition effect. The formation mechanism of nanoparticles synthesized by induction thermal plasma has already been investigated by experiments and simulations [23,24]. Synthesis of nanoparticles by induction thermal plasma contains three main process including homogeneous nucleation, heterogeneous condensation, and coagulation.

Nucleation temperature of each species in Li-Al-O system is investigated in order to identify

the nucleation phase. There is no solid interface that exists during plasma process, the nucleation is considered homogeneous. Homogeneous nucleation temperature of elementary substance is estimated by Eqs. (2.3) - (2.6).

The nucleation temperature of Al and Li is obtained based on above equations with 300 mg/min feeding rate. **Figure 4.13** presents the nucleation temperature, melting point, and boiling point of the main composition in Li-Al-O system. The melting point and boiling point are obtained from Lang's Handbook of Chemistry [25]. Nucleation temperature of aluminum and lithium are 1056 K and 1616 K, respectively. Melting point is regarded as the nucleation temperature of oxides because of the similar value of two temperature and the thermal data limitation of oxides [26]. The highest nucleation temperature is occupied by Al₂O₃ according to **Fig. 4.13**, indicating that Al₂O₃ is the nucleation phase in Li-Al-O system. In addition, homogeneous nucleation occurs when vapor achieves supersaturation. The nucleation phase is also affected by the partial pressure of each vapor during plasma process besides nucleation temperature.

Thermodynamic equilibrium composition of Li-Al-O system during the plasma process was investigated in order to understand partial vapor pressure. **Figure 4.14** is the estimated result of thermodynamic equilibrium composition of Li-Al-O system with following experiment conditions. The feeding rate and value of Li/Al are 300 mg/min and 5, sheath gas is the mixture of Ar and O₂ with molar ratio of 57.5:2.5. **Figure 4.14** demonstrates aluminum exists as AlO vapor and AlO₂ vapor in high temperature region. The Al₂O₃ is synthesized by AlO and AlO₂ vapor when temperature decreases to around 3000 K, the reaction is presented in **Eq. 4.3**. Simultaneously, the Al₂O₃ vapor achieves supersaturation and starts to nucleate. Lithium exists as Li vapor and LiO vapor at high temperature. The nucleation phase can be identified as Al₂O₃ around 3000 K combining the nucleation temperature with equilibrium composition.

$$AlO(g) + AlO_2(g) \rightarrow Al_2O_3(l)$$

$$(4.3)$$

The formation mechanism of lithium aluminate is put forward based on the above discussion, the illustration is presented in **Fig. 4.15**. Raw material consisting of Li_2CO_3 and α -Al₂O₃ is injected into plasma and decomposes immediately. Then the vapor phase reactions start among different vapors to form AlO, AlO₂, and LiO vapor. Particles collide with each other and flow to the downstream region with lower temperature. The AlO reacts with AlO₂ to synthesize Al₂O₃ when temperature declines to around 3000 K, simultaneously, the Al₂O₃ achieves supersaturation and starts to nucleate. Heterogeneous co-condensation starts as soon as nuclei occur. Vapor of Li and LiO condense on the nuclei to synthesize into lithium aluminate during this process.

Various lithium aluminate nanoparticles are mainly synthesized at different stages of condensation due to the discrepancy in saturation ratios [27]. The Al-rich particle LiAlO₂ is mainly synthesized at early-stage of condensation owing to the higher saturation ratio of Al₂O₃. The Li and LiO condensation become dominant gradually with consumption of Al₂O₃ and temperature decrease. The Li and LiO vapor start to more rapidly condense on the Al-rich particle LiAlO₂ than Al₂O₃ vapor to form Li-rich particle Li₅AlO₄. Namely, the Li-rich particle Li₅AlO₄ is mainly synthesized at following-stage of condensation. **Equations 4.4** and **4.5** display the reactions for early- and following- stage of condensation, respectively. The condensation is terminated by solidification of all condensation phases in Li-Al-O system. Nanoparticles grow continuously by coagulation.

$$Al_2O_3(l) + LiO(g) + Li(g) \rightarrow 2LiAlO_2(l)$$

$$(4.4)$$

$$LiAlO_{2}(l)+2LiO(g)+2Li(g)\rightarrow 2Li_{5}AlO_{2}(l)$$

$$(4.5)$$

The rapid quenching rate prevents particle orderly grow during the plasma process, and the amorphous structure is achieved in products. Those unreacted LiO and Li vapor are oxidized into Li₂O and react with H₂O and CO₂ in atmosphere during collection, then form into by-product Li₂CO₃.

4.3.2 Transformation Between [AlO₆] and [AlO₄]

Octahedron [AlO₆] and tetrahedron [AlO₄] are two main aluminate units for lithium aluminate, they affect crystalline and amorphous structure of products. Structure of aluminate unit relates to O/Al molar ratio and temperature distribution closely [28]. The value of O/Al molar ratio is less than 2 in system, namely, oxygen is deficiency, the aluminate unit prefers to form face- or edgeshared [AlO₆] at a same temperature distribution [4,29]. These connection conditions result in the low flexibility of structure, further tending to order structure formation. The [AlO₆] transforms to [AlO₄] with O/Al molar ratio increasing. The lower limit of O/Al is 2 for aluminate lithium consisted by corner-shared [AlO₄]. The higher flexibility and lower Al coordination number lead to the network consisting of [AlO₄] tetrahedron easily achieving disorder, further acquiring amorphous structure under rapid quenching rate. Therefore, promotion of [AlO₄] formation is beneficial to amorphous nanoparticle synthesis in Li-Al-O system.

Nucleation phase is Al₂O₃ in this experiment, the [AlO₆] is formed firstly due to the oxygen deficiency. The O/Al molar ratio increases with the LiO condensing on Al₂O₃ nuclei, allowing the [AlO₆] transforms to [AlO₄]. **Figure 4. 16** displays the aluminate transformation process with O/Al molar ratio increase in amorphous lithium aluminate. The aluminate experiences a transformation from [AlO₆] to [AlO₄] at initial to form LiAlO₂, then Li₅AlO₄ is synthesized by continuously LiO condensation. Promotion of LiO vapor condensation conducive to [AlO₄] and Li₅AlO₄ formation during condensation process. The product structure would possess higher flexibility owing to enhanced corner-shared [AlO₄] percentage and preserve the disorder after plasma process. Meanwhile, these more synthesized Li₅AlO₄ achieve the amorphous structure under the rapid quenching rate of thermal plasma. Improved LiO condensation can be achieved by high Li/Al molar ratio because of higher LiO saturation ratio. Thus, enhanced amorphous degree of products and Li₅AlO₄ are obtained in high Li/Al molar ratio cases.

Quenching gas injection sharps the temperature gradient, the quenching rate increases from 3.2×10^4 K/s to 1.5×10^5 K/s with quenching gas flow rate increasing from 0 L/min to 20 L/min. This steeper temperature gradient can advance and promote the following-stage of condensation. Because the duration of early-stage condensation would be suppressed by steeper temperature gradient, simultaneously, the LiO more early reaches supersaturation state and more LiO participate in reaction. Above phenomenon facilitates the Li-rich Li₅AlO₄ synthesis and reduces the Li₂CO₃ and LiAlO₂ formation. However, the steeper temperature gradient also shortens the transformation time from [AlO₆] to [AlO₄]. These untransformed [AlO₆] exist as amorphous in products due to the enhanced quenching rate. Therefore, more amorphous Li₅AlO₄ nanoparticles are obtained at higher flow rate of quenching gas, while, increased [AlO₆] is also detected.

Enhanced amorphous Li₅AlO₄ degree is achieved by high Li/Al molar ratio and quenching rate.

Because the improved LiO condensation contributes to [AlO₄] and Li₅AlO₄ formation.

4.4. Conclusion

Amorphous Li₅AlO₄ nanoparticles were synthesized by induction thermal plasma successfully. Formation mechanism, quenching gas effect and Li content effect were investigated based on experiment results and thermodynamic analysis.

Enhanced amorphous Li₅AlO₄ degree was obtained at high quenching gas flow rate and Li/Al molar ratio. The LiO-dominant condensation is promoted by the higher quenching gas flow rate and Li/Al molar ratio. This situation benefits transformation of aluminate from [AlO₆] octahedron to [AlO₄] tetrahedron and synthesis of Li-rich nanoparticle Li₅AlO₄. Enhanced [AlO₄] percentage allows product structure to own higher flexibility and more easily achieve amorphous structure after plasma process. Promoted Li₅AlO₄ achieves amorphous structure under the rapid quenching rate. While the excessive quenching gas flow rate shortens transformation time resulting in increased [AlO₆] existing in products.

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Parameter	Condition
Input power [kW]	20
Pressure [kPa]	101.3
Frequency [MHz]	4
Sheath gas rate [L/min]	60 (Ar+O ₂)
Inner gas rate [L/min]	5 (Ar)
Carrier gas rate [L/min]	3 (Ar)
Quenching gas rate [L/min]	0, 10, 20 (Ar)
Feed rate [mg/min]	300
Ar/O ₂ molar ratio [-] Li/Al molar ratio [-]	57.5:2.5 5:1, 5.25:1, 5.75:1

 Table 4.1. Experimental conditions for induction thermal plasma system.



Fig. 4.1. Schematic diagram of amorphous Li₅AlO₄ synthesized by induction thermal plasma.


Fig. 4.2. TEM photographs of products synthesized by different quenching gas flow rates (a) 0 L/min, (b) 10 L/min, (c) 20 L/min. The red square is the focus of the electron beam on product. The corresponding diffraction pattern is shown in (d).



Fig. 4.3. Diameter distributions of products synthesized without quenching gas flow. Inserts indicate the average diameters of products estimated by countering more than 200 different particles.



Fig. 4.4. XRD spectra of products synthesized by different quenching gas flow rates. Blue round, yellow round and orange square represent Li_2CO_3 , Al_2O_3 and γ -LiAlO₂, respectively.



Fig. 4.5. Estimated amorphous degree of collected particles and Li₅AlO₄ synthesized by different quenching gas flow rates. The error bars represent the standard errors of the corresponding average.



Fig. 4.6. Schematic diagram of (a) [AlO₆] octahedron and (b) [AlO₄] tetrahedron.



Fig. 4.7. Raman spectra of products synthesized by different quenching gas flow rates. (a) 0 L/min, (b) 10 L/min, (c) 20 L/min. Gray dots line is the experimental results, the blue line is the cumulative fitting.



Fig. 4.8. The relative amounts of different aluminate units and CO_3^{2-} in products synthesized by different quenching gas flow rates. The error bars represent the standard errors of the corresponding average.



Fig. 4.9. TEM photographs of products synthesized by different Li content in raw material (a) Li:Al = 5:1, (b) Li:Al = 5.25:1, (c) Li:Al = 5.75:1.



Fig. 4.10. XRD spectra of products synthesized by different Li contents in raw material. Blue round, yellow round and orange square represent Li_2CO_3 , Al_2O_3 and γ -LiAlO₂, respectively.



Fig. 4.11. Estimated amorphous degree of collected particles and Li₅AlO₄ synthesized by different Li content in raw material. The error bars represent the standard errors of the corresponding average.



Fig. 4.12. The relative amounts of different aluminate units and CO_3^{2-} in products synthesized by different Li contents in raw material. The error bars represent the standard errors of the corresponding average.



Fig. 4.13. The melting, boiling, and nucleation temperature of Al, Li, and oxides.



Fig. 4.14. Thermal equilibrium of the Li-Al-O system. Feeding rate is 300 mg/min with Li/Al molar ratio 5/1, Ar/O₂ molar ratio is 57.5/2.5.



Fig. 4.15. Formation mechanism of lithium aluminate nanoparticles synthesized by induction thermal plasma.



Fig. 4.16. Aluminate unit transformation process with O/Al molar ratio increase in amorphous lithium germanate.

5. Formation Ability of Amorphous Nanoparticles with High Li Content

Amorphous Li₃BO₃, Li₄GeO₄, and Li₅AlO₄ nanoparticles were synthesized successfully by induction thermal plasma. Since the physical and chemical properties of elements in three systems are different, further leading to the vapor reactions, nucleation phase, condensation phase, structure unit transformation and time lag of condensation are different. A huge discrepancy was observed in the experiment results of three systems at the same experiment conditions. The reason for this discrepancy should be studied in order to summarize the formation ability of amorphous nanoparticles synthesized by induction thermal plasma. The formation ability can be discussed from structure and chemical composition because the target materials possess amorphous structure and high Li content simultaneously in this experiment.

This chapter mainly focuses on investigating the formation ability of amorphous nanoparticles with high Li content. The formation ability was discussed from amorphous structure and chemical composition of products, based on summarization and comparison of the experiment results of three systems.

5.1 Summarized Experiment Results of Three Systems

Figure 5.1 (a)-(c) shows the summarized experiment results for Li-B-O, Li-Ge-O, and Li-Al-O systems. This result is obtained with the following experiment conditions. Raw material molar ratio of Li and glass former atom is stoichiometric with target material, sheath gas is the mixture of Ar and O_2 with molar ratio of 57.5:2.5, no quenching gas injection during plasma process.

Figure 5.1 (a) displays the amorphous degree of products in three systems. The Li-B-O system is the most easily to form amorphous nanoparticles among three systems, around 60% of product exist as amorphous structure. The amorphous degree of target compound for three systems is presented in **Fig. 5.1 (b)**, only around 20% of amorphous target compound is obtained in Li-Ge-O, showing the lowest value among the three systems. The Li-Al-O system occupies the highest

value in amorphous degree of target compound, although the Li-B-O system has a higher amorphous product degree. This phenomenon demonstrates more amorphous by-products existing in Li-B-O system. Chemical composition in products is also compared, and the result is shown in **Fig. 5.1 (c)**. The Li-Ge-O shows the highest uniformity in product chemical composition, around 90% of product is the target compound although most of them exist as crystalline.

5.2 Formation Ability of Amorphous Structure

5.2.1 Effect of Li content

The basic unit of network of amorphous nanoparticles is the oxide polyhedron which consists of a center atom and oxygen atoms. The center atom is usually glass former. These polyhedrons are connected randomly and disorderly by corner to form the network. The relative orientations between corner-shared polyhedrons vary within a wide range, which results in the long-range order absence in amorphous material [1]. Term topological disorder is used to describe such network structure, that is, the structure of amorphous material lacks periodic and orientational order in the long-range [2]. In addition, the polyhedrons that consisting network are regular, congruent and rigid due to the short-range order in amorphous [3]. Cations locate in the holes of topologically disorder networks, the cation refers to lithium in this dissertation. An illustration of topological disorder network is presented in **Fig. 5.2**.

Connectivity and network structure are broken gradually through nucleophilic substitution with lithium oxide addition, further, the amorphous structure is destroyed. [4]. **Figure 5.3** presents the process of breakdown of the bridge oxygen BO bond by nucleophilic substitution. Since the electronegativity between glass former and oxygen in polyhedron is different, the electronic cloud is closer to the oxygen atom. The chemical bond in polyhedrons is polar covalent bond. This phenomenon leads to the glass former atom showing positive valence and the oxygen showing negative valence. Lithium oxide as an ionic compound consists of Li⁺ and O²⁻. The O²⁻ in Li₂O more easily offers electrons for glass former compared to O in polyhedron. The glass former and O²⁻ in Li₂O is formed, then a BO bond and a Li-O bond are broken. The leaving Li⁺ combines with

leaving polyhedron to form a new ionic bond to achieve the system charge balance.

The material tends to form crystalline gradually with Li₂O addition due to the number of ionic bonds increasing. Because the ionic bond is non-directional, the activation energy of crystallization is low. Hence, crystal formation ability is enhanced with Li₂O content increasing, the compound with high Li content prefers to form crystalline structure. The rapid quenching rate can prevent the crystallization process and the amorphous structure is obtained in products.

5.2.2 Effect of Bond Strength

Maintenance of topological disorder network with Li₂O addition benefits synthesis of amorphous according to previously discussed. Namely, a strong network can decrease the fragility of amorphous.

The network skeleton is constructed by oxide polyhedrons. The strong bond allows the network to be rigid, and the system maintains a higher level of connectivity after Li₂O addition [5]. This situation leads to the molten occupying high viscosity, further impeding the diffusion of molecules in molten and enhancing the activation energy of crystallization. Amorphous nanoparticles with high Li content can be synthesized under above conditions. Thus, the bond strength is an index to describe the formation ability of amorphous structure.

Table 5.1 summarizes the polyhedrons and corresponding bond strength in three systems. The B-O bond in [BO₃] triangle occupies the highest value of 498 kJ/mol, a slightly lower value of 423 kJ/mol is observed in Al-O bond in [AlO₄] tetrahedron, while the Ge-O bond in [GeO₄] tetrahedron has an obviously lower bond strength of 340 kJ/mol [6,7]. This phenomenon indicates the topological disorder network in Li-Ge-O is the most fragile, and more difficult to obtain amorphous at the same quenching rate contrasted to Li-B-O and Li-Ge-O. The order of bond strength corresponds to the amorphous degree of collected powder.

5.2.3 Effect of Degree of Freedom

Since amorphous is characterized by topologically disorder, amorphous formation ability can be described as degrees of freedom of the infinite large network with topologically disordered [2]. This network should be composed of oxide polyhedrons connected by corners, edges, or faces.

Since the constraints of polyhedron rigidity and the requirement of connectivity at the vertices are severe, the topologically disordered network is difficult to achieve infinitely large. The net degree of freedom, f, per vertex is introduced to describe amorphous formation ability for different systems. The net degree of freedom per vertex is given by the discrepancy between network dimension, d, and number of constraints per vertex, h, based on the rigidity and connectivity of polyhedrons, and is expressed in **Equation 5.1**. Topologically disorder network with infinite large is constructed when f is nonnegative, that is, the amorphous structure can be obtained with nonnegative f.

$$f = d - h \tag{5.1}$$

here, the number of constraints per vertex h is given by

$$h = \delta V - \frac{\delta(\delta + 1)}{2} \tag{5.2}$$

where δ is the dimensionally of polyhedrons, V is vertex number of per polyhedrons. The number of polyhedrons sharing a vertex, C, is referred to as the connectivity of network. Since the connectivity of vertexes is dependent on the number and types of connected polyhedrons. As previously discussed, there is only one kind of polyhedron in every system. Therefore, the f can be expressed by

$$f = d - C \left\{ \delta - \left[\frac{\delta(\delta + 1)}{2V} \right] \right\}$$
(5.3)

The state of system can be classified into three types according to the value of f[8]. If f < 0, the system is overconstrained and cannot form topologically disordered network. Because additional rigidity would result in localized stress, crystalline order is rapid arranged aiming to eliminate the localized stress. Isostatic state is achieved when f = 0, system is optimally constrained, meaning the system is rigid but free of stress. The condition for amorphous formation will be optimal when the network is isostatic. The system would gradually transform to floppy state with value of f > 0, the system shows disorder due to lack of constraints and the disordered structure can be maintained by the rapid quenching rate. However, the lack of constraints allows the atoms tend to arrange themselves into the crystalline order with minimum energy. Hence, the topologically

disordered network arrives in infinite large when value of f is nonnegative.

Table 5.2 presents the estimated results for Li-B-O, Li-Ge-O, and Li-Al-O systems. The Li-B-O system owns higher possibility to build topologically disordered network with infinite large contrasted to Li-Ge-O and Li-Al-O system. Hence, the Li-B-O system occupies the high amorphous degree of the collected powder among three systems at the same quenching rate.

5.2.4 Effect of Configuration Entropy

The structure discrepancy between melt and solid is another factor to amorphous formation ability. Amorphous more easily form in a region which there is an obvious configuration entropy between melt and solid. The increased configuration entropy can rise the energy barrier for crystallization, allowing the system to tend to form amorphous [9].

An enhanced amorphous formation ability is observed near the eutectic point in various systems [10]. There is a structure competition exist around eutectic point, and the higher configuration entropy is achieved. The enhanced crystallization energy barrier in the region near the eutectic point impairs crystallization and benefits amorphous formation. In addition, the large configuration entropy can decrease the melt fragility and amorphization dynamic becomes higher, which contributes to acquire amorphous [11]. Therefore, amorphous formation ability is increased near the eutectic point.

The phase diagram of Li-B-O, Li-Ge-O, and Li-Al-O systems is presented in **Fig. 5.4** [12,13]. The Li₅AlO₄ is near the eutectic point while the Li₃BO₃ is far away from the eutectic point. The amorphous Li₅AlO₄ is more easily obtained compared to amorphous Li₃BO₃ at the same quenching rate based on the configuration entropy viewpoint. In addition, the amorphous Li₅AlO₄ can be fabricated by the twin roller quenching method, while amorphous Li₃BO₃ cannot be obtained [14,15]. This situation also indicates the amorphous Li₅AlO₄ owns the lower critical quenching rate contrast to amorphous Li₃BO₃, and provides the powerful evidence to configuration entropy viewpoint.

5.3 Formation Ability of Li-containing Compounds

5.3.1 Effect of Condensation Time Lag

Synthesis of nanoparticles by induction thermal plasma is a bottom to top approach. The complete decomposition of raw material leads to various chemical reactions during plasma process compared to other synthesis methods. The compounds are majorly synthesized during co-condensation process according to formation mechanism. Namely, the chemical composition of product is mainly controlled by condensation during plasma process.

The products tend to own a uniform chemical composition when the time lag of condensation is small [16,17]. Condensation is driven by supersaturation ratio. There is a discrepancy among the various vapors in condensation rate at the same temperature because of the different supersaturation ratios [18]. The high supersaturation ratio of vapor leads to rapid condensation rate, further promoting more vapor to take part in chemical reactions. This dominant state will be replaced by the reduction in the supersaturation ratio caused by continued consumption and the attainment of supersaturation by other vapors. New chemical reactions will also replace the original ones. Hence, diverse compounds would be detected in the final product. The short time lag of condensation allows simultaneous condensation to occur among various vapors, the product consisting of the uniform compound is obtained due to the single chemical reaction.

The co-condensation starts as soon as nuclei are generated and terminated by the solidification of each species. **Figure 5.5** displays the condensation process of Li-B-O, Li-Ge-O, and Li-Al-O system, indicating the temperature ranges of co-condensation are 1700 K-1000 K, 1700 K-1300 K, and 3000 K-1700 K for Li-B-O, Li-Ge-O, and Li-Al-O systems, respectively. The shortest temperature range is occupied by Li-Ge-O system, indicating the Li-Ge-O system has the shortest time lag of condensation. This situation contributes to simultaneous condensation among different vapors, and uniform product is obtained. The chemical composition of Li-Ge-O system product would have the highest uniformity among three systems, which is corresponding to experiment result shown in **Fig. 5.1** (c).

5.3.2 Effect of Structure Unit Transformation

Figure 5.1 (a)-(c) reveals that more amorphous by-products exist in product in Li-B-O system

This situation can be explained by the structure unit transformation during condensation. Lithium content in a system affects the structure units that build the compounds. Since the target compounds in three systems contain the highest Li content in the corresponding system. The target compounds are all acquired after a series of unit transformation according to the formation mechanism. The unit transformation process for Li-B-O, Li-Ge-O, and Li-Al-O systems is presented in **Fig. 5.5**. The Li₃BO₃ is synthesized after a complex series of borate unit transformation with Li₂O increase. Borate units exist in the order of BO₂⁻, B₄O₉⁶⁻, B₂O₅⁴⁻ to BO₃³⁻ with Li₂O addition. The Li₅AlO₄ is synthesized after experiencing the aluminate transformation from [AlO₆] octahedron to [AlO₄] tetrahedron with Li₂O increase. There is no structure unit transformation in Li-Ge-O system.

The rapid quenching rate results in parts of Li₂O solidification before condensation, the intermediates are synthesized due to the incomplete unit transformation. These intermediates are solidified by the rapid quenching rate and exist as by-products. The complex transformation in the Li-B-O system enhances the possibility of intermediates synthesis. The unit transformation process is accompanied by the old chemical bond breakdown and new chemical bond formation. The higher bond energy of B-O also increases the energy barrier for structure unit transformation. In addition, the by-products in Li-B-O are more easily to form amorphous compared target compound Li₃BO₃ due to the lower Li content. These by-products exist as amorphous in product, further reducing the amorphous Li₃BO₃ degree. Thus, more by-products were detected in the Li-B-O system.

5.4 Conclusion

The formation ability of amorphous nanoparticles with high Li content synthesized by induction thermal plasma was investigated from the amorphous structure and chemical composition. The topological disorder network is destroyed by nucleophilic substitution with Li₂O addition. Strong bonds contribute to the system forming amorphous structure under high Li content condition. Uniform product is achieved by the system with short time lag of condensation because of the simultaneous condensation of each species. The simple structure unit

transformation during condensation also reduces by-product formation.

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Bond (polyhedron)	Bond energy (kJ/mol)		
B-O ([BO ₃] triangle)	498		
Ge-O ([GeO ₄] tetrahedron)	340		
Al-O ([AlO ₄] tetrahedron)	423		

Table 5.1 Bond energy for Li-B-O, Li-Ge-O and Li-Al-O systems.

polyhedron	δ	V	d	С	f
triangle (BO ₃)	2	3	2	2	0
	2	3	3	3	0
	2	3	3	2	1
tetrahedron (GeO4, AlO4)	3	4	3	2	0
octahedron (AlO ₆)	3	6	3	2	-1

Table 5.2 The degree of freedom, f, in Li-B-O, Li-Ge-O, and Li-Al-O systems



Fig. 5.1. Summarized experiment results for Li-B-O, Li-Ge-O, and Li-Al-O systems. (a) amorphous degree of products, (b) amorphous degree of target compound, (c) total percentage of amorphous and crystalline target compound.



Fig. 5.2. Illustration of topological disorder network.



Fig. 5.3. Illustration of bridge oxygen bond breakdown with Li_2O addition.



Fig. 5.4. Phase diagram for (a) Li-B-O, (b) Li-Ge-O, and (c) Li-Al-O system.



Fig. 5.5. Temperature range and unit transformation process of co-condensation for Li-B-O, Li-Ge-O, and Li-Al-O system.

6. Conclusions

6.1 Summary and Conclusion

This dissertation mainly concentrates on the synthesis of amorphous oxide nanoparticles as solid electrolytes by induction thermal plasma. The amorphous Li₃BO₃, Li₄GeO₄, and Li₅AlO₄ nanoparticles were selected as target material because of the good glass formers and high Li content. Various experiment conditions were implemented aiming to improve product properties. The products were analyzed with different analytic methods to characterize properties, including morphology, size distribution, phase identification, amorphous degree, structure unit distribution. Formation mechanism and experiment condition effect were investigated based on thermodynamic analysis, topological order, structure unit transformation and experiment results. Formation ability of amorphous nanoparticles with high Li content is summarized from the amorphous structure and chemical composition of products. The main conclusion remarks are drawn as follows:

In **chapter 1**, the characteristics and applications of thermal plasma were generally reviewed. All-solid-state battery and related battery materials were also introduced. The superiorities and shortcomings of different solid electrolytes have already been summarized and listed. The stable electrochemical property, sufficient structure defects and nanoscale allow amorphous oxide nanoparticles to outstanding out from other materials for solid electrolytes. However, the conventional fabrication methods for amorphous oxide nanoparticles are complex and timeconsuming. Induction thermal plasma is considered an efficient and advanced method, the successful synthesis of various amorphous nanoparticles identified this consideration. Therefore, this dissertation aims to apply RF induction thermal plasma to synthesize amorphous oxide nanoparticles as solid electrolytes for all-solid-state battery.

In **chapter 2**, amorphous Li₃BO₃ nanoparticles were synthesized successfully by RF induction thermal plasma, the oxygen flow rate effect, quenching gas effect and formation mechanism were investigated based on thermodynamic analysis and experiment results. The amorphous Li₃BO₃

degree reaches around 41% and 42% with 5 L/min O_2 and 40 L/min Ar quenching gas, respectively. The sharper temperature gradient is achieved by higher O_2 and quenching gas flow rate. This phenomenon allows smaller size nuclei generation and prevents particles grow orderly, the enhanced amorphous Li₃BO₃ degree is achieved.

Lithium borate nanoparticles are obtained after Li₂O nucleation, Li₂O and LiBO₂ cocondensation, and coagulation. Target material Li-rich Li₃BO₃ is mainly synthesized at early stage of condensation after a series of borate unit transformation because of the supersaturation ratio discrepancy between Li₂O and LiBO₂. The by-product B-rich Li₆B₄O₉ and Li₄B₂O₅ are mainly synthesized at the following stage of condensation. Enhanced quenching rate impedes Li₂O condensation and completed borate unit transformation, further resulting in less synthesis of Li₃BO₃.

In chapter 3, amorphous Li_4GeO_4 nanoparticles were synthesized through various experiment conditions, including different O_2 flow rates, different Li/Ge molar ratios, different carrier gas, and quenching gas flow rates. The formation mechanism was investigated based on thermodynamic analysis and experiment results. There is a discrepancy in supersaturation ratio of Li_2O and GeO vapor at the same temperature region, the Li-rich Li_4GeO_4 and Ge-rich Li_2GeO_3 nanoparticles are mainly synthesized at early and following stage of condensation, respectively. While the excessive Ge content and quenching rate promote following stage of condensation, resulting in more by-product Li_2GeO_3 formation.

The topological order of prepared nanoparticles was discussed in short-range order (SRO) and intermediate-range order (IRO) based on O-Ge-O and Ge-O-Ge angle distribution, respectively. Increased Ge content and quenching rate contribute to high temperature phase γ -Li₄GeO₄ and amorphous Li₄GeO₄ synthesis. Amorphous Li₄GeO₄ degree is around 65% in 10 L/min quenching gas flow rate. The enhanced quenching rate allows the broaden intratetrahedron O-Ge-O and intertetrahedron Ge-O-Ge angle distribution to be preserved, which achieves more chaos in SRO and IRO. The increased Ge molar amount in raw material also enlarges the intratetrahedron O-Ge-O angle distribution and increases chaos in SRO. The increased disorder in SRO and IRO leads to higher amorphous Li₄GeO₄ degree. In **chapter 4**, amorphous Li₅AlO₄ nanoparticles were prepared by induction thermal plasma by different quenching gas flow rates and Li/Al molar ratios in raw material. The formation mechanism was studied based on thermodynamic analysis and experiment results. The [AlO₆] octahedron and [AlO₄] tetrahedron transformation and distribution were understood according to O/Al molar ratio and temperature distribution. The Al₂O₃ nuclei occur as soon as the reaction between AlO vapor and AlO₂ vapor starts. The [AlO₆] octahedrons are formed first due to the low O/Al molar ratio. Target material Li-rich Li₅AlO₄ nanoparticles are mainly obtained at following stage of condensation with continued LiO condensation after aluminate transformation from [AlO₆] to [AlO₄].

Enhanced amorphous Li₅AlO₄ degree was acquired in high quenching rate and Li/Al molar ratio cases. The highest amorphous Li₅AlO₄ degree is around 82% in the 20 L/min quenching gas case. The higher quenching rate and Li/Al molar ratio benefit Li-rich Li₅AlO₄ synthesis due to the promoted LiO condensation. These synthesized Li₅AlO₄ achieve amorphous under rapid quenching rate. However, the transformation time of aluminate unit is shortened by higher quenching rate, resulting in more [AlO₆] octahedrons remaining in products.

In **chapter 5**, the formation ability of amorphous nanoparticles with high Li content synthesized by induction thermal plasma was studied. Amorphous structure and chemical composition of products were discussed to understand formation ability, based on the comparing and summarizing experiment results of Li-B-O, Li-Ge-O, and Li-Al-O systems. The amorphous nanoparticles are more easily obtained in a system containing strong chemical bonds. The topological disorder network in amorphous material is destroyed by nucleophilic substitution with Li₂O continued addition. The strong bonds in a system can resist the Li₂O attack, and decrease the destruction of topological disorder network. The products with higher uniformity are acquired by a system that has shorter condensation time lag and simple structure unit transformation. The short time lag of condensation leads to uniform chemical composition in product due to the simultaneous condensation of each species. The simple transformation of structure unit decreases the occurrence possibility of by-products and benefits target material formation.

In summary, the above experiment results provide a deep understanding for the synthesis of

amorphous oxide nanoparticles with high Li content by induction thermal plasma from the points of formation mechanism, experiment conditions effect and raw material property. This dissertation offers an advanced and efficient fabrication method for solid electrolytes and promotes the development of ASSBs with high-performance.

6.2 Future Works

Amorphous oxide nanoparticles were synthesized as solid electrolytes by induction thermal plasma in this dissertation, some improvements are put forward as follows aiming to elevate solid electrolytes development.

6.2.1 Decrease By-product Formation

The experiment results reveal the enhancement of amorphous degree accompanied by more byproduct synthesis in Li-B-O and Li-Ge-O systems. The deeper study of operation parameters should be implemented in order to higher purity products. New attempts can be tried, such as adjustment of the ratio of tangential and radial gas flow rate in sheath gas. The plasma shape can be changed with different ratio values, which further affects temperature distribution in chamber. Other types of sheath gas are also considered as another improvement direction because the different thermal conductivity also leads to temperature distribution diversification.

The agglomerates were obtained in current experiments, which results in difficulty estimating diameter distribution. The rapid coagulation among nanoparticles causes agglomerate formation. New quenching gas configuration, such as radial-top quenching and radial-bottom quenching, can be attempted.

6.2.2 Effect of Mix Glass Former

High Li ion conductivity is a significant requirement for the high-performance solid electrolyte. The introduction of another type of glass former into system can increase the ion conductivity obviously. Heteroatom bonds would be formed in the system after the introduction of another glass former, which allows more BOs to occur. The formation of BOs bond can provide ionic vacancies for Li ion migration, simultaneously, also can broaden the migration channels of Li ion. The density of amorphous solid electrolyte is reduced and the structure becomes loose, which is beneficial to Li ion migration in the system. In addition, the phase separation also occurs with Li content increase in system. The network that owns higher Li ion conductivity coats on the network with lower conductivity, this situation allows Li ions to migrate easily. Moreover, the enhanced conductivity can be achieved by addition of glass intermediate to lead to the ceramic-glass structure, because the formation of polyhedrons can modify the network.

In the future, the xLi₂O-yB₂O₃-(1-x-y)GeO₂ system and xLi₂O-yB₂O₃-(1-x-y)Al₂O₃ system can be selected as the target material due to the mixed glass former effect. The glass former effect can be investigated by adjusting the value of x and y according to amorphous degree and product composition, the temperature distribution effect can be investigated by adjusting quenching gas flow rates.

6.2.3 Electrochemical Property

The products in this dissertation are applied as solid electrolytes. The electrochemical property, such as ion conductivity at different temperatures, life-span, impedance, electrochemical stability, interface reactions, and so on, should be understood clearly. Characteristic of the properties of prepared nanoparticles for solid electrolytes through comparing the electrochemical performance, in order to decide the future research direction. Galvanostatic cycling test for the symmetric Li/prepared nanoparticle/Li to investigate the lithium dissolution and deposition to understand the electrochemical stability. Ion conductivity and impedance tests can be carried out by an electrochemical platform.
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