Metastable Materials for All-Solid-State Batteries

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ABSTRACT

Materials with metastable structures often exhibit high stability up to a certain temperature, despite not being thermodynamically stable. Therefore, it is important to use the excellent physical properties generated by metastable structure. Secondary batteries are an energy device that stores chemical energy by producing thermodynamically metastable materials. Metastable materials can also be directly utilized as the electrode active materials and the solid electrolytes. The rapid quenching and mechanochemical processes are useful to obtain room temperature metastable materials. This review provides an overview of our research progress on glassy and metastable crystalline materials for all-solid-state batteries.

Keywords : Metastable, All-solid-state Battery, Solid Electrolyte, Electrode Active Materials

1. Introduction

Materials with metastable structures often exhibit high stability up to a certain temperature, despite not being thermodynamically stable. Representative materials that are metastable at room temperature are crystals with a high-temperature stable phase. In general, the high-temperature phase tends to have a more symmetric but less ordered arrangement of atoms and ions than the low temperature phase. These features have a significant impact on material properties, such as ionic conduction and electrode properties, which are important in battery materials.

In general, stable phases are obtained by a solid-phase reaction with a high-temperature heat treatment. Glasses are prepared by melting and quenching. Freezing the high temperature stable phase by rapid quenching is a useful technique to obtain phases that are metastable at room temperature.1

Mechanochemical processes are also useful for preparing glasses and metastable crystalline phases. Mechanochemical synthesis uses a chemical reaction by mechanical energy, such as a ball milling. Mechanochemical treatments are often used as miniaturization or chemical reaction on the surface in powder processing. On the other hand, in the case of high-energy mechanochemical treatments and/or exothermic reactions, bulk chemical reactions such as compounding, amorphization, and crystal phase transitions occur. Since the 1990s, we have used mechanochemical methods to synthesize battery materials such as solid electrolytes and electrode active materials.2-3

This review provides an overview of our research progress on glassy and metastable crystalline materials for all-solid-state batteries.

2. Glassy Solid Electrolytes

In general, the ionic conductivity of glassy materials is higher than that of the corresponding crystalline material.4-6 The advantage of glasses in ionic conduction is explained by the structure of the glass; the glass structure is similar to the structure of the corresponding melt, which has high conductivity and low activation energy for ionic conduction because of the large free volume. A wide selection of compositions, isotropic properties, and the absence of crystal grain boundaries are representative advantages of glass materials. The conductivity of AgI-Ag2O-P2O5 glasses is 10⁻² S cm⁻¹ at ambient temperature, which is higher by one or two orders of magnitude than the conductivity of the corresponding crystalline materials.5 These glasses are named “superionic conducting glasses”. The excellent conductivity of glasses makes them promising materials to use in solid electrolytes. Generally, it is effective to synthesize a solid electrolyte having a composition with a high carrier ion concentration. The ionic conductivities of glass electrolytes increase as the concentration of carrier ions increases. However, samples with a high cation concentration tend to be difficult to prepare as glasses. Compositions with a very high concentration of cations do not have a covalent chain network as a
local structure; all constituent units in such compositions are polyatomic ions, which means that the obtained glasses are ionic glasses. With such a composition, the stability of the supercooled liquid is poor and crystallization occurs easily. Thus, special methods described as follows should be used for ionic glasses. Twin-roller rapid-quenching are powerful tools for this purpose. Mechanochemical synthesis using high energy ball milling is another powerful tool used to prepare ionic glasses. A representative example is Li1PS4 glass (75Li2S·25P2S5 (mol%) glass). Preparation of the Li1PS4 glass in the ortho composition by the melt-quenching method is difficult, but it becomes possible using a mechanochemical method.3 Besides sulfides, other novel amorphous materials, including oxides (e.g. Li2.33B0.33C0.33S0.33O3.33) and nitrides (e.g. Li3BN3 glass11 and Li2CN2 glass12) have been found to exhibit higher ionic conductivity than the corresponding crystalline materials.

Here, examples of mechanochemical synthesis conditions useful for synthesizing glassy electrolytes are shown. The conditions such as the disc speed need to be set according to the purpose. As an example, our standard conditions for synthesizing sulfa
des, other novel amorphous materials, including oxides (e.g. Li2.33B0.33C0.33S0.33O3.33) and nitrides (e.g. Li3BN3 glass11 and Li2CN2 glass12) have been found to exhibit higher ionic conductivity than the corresponding crystalline materials.

3. Metastable Phases in Electrolytes

As an exceptional case, crystal materials with a superionic conducting phase show higher conductivities than glasses. Super-ionic conducting phases are often metastable. Crystallization of glasses by heating often leads to the formation of metastable or a high-temperature stable phases that exhibit high ionic conductivity. The high ionic conductivity arises because the metastable phase tends to have a larger molar volume, which allows ions to move easily in the solid, and a high symmetric crystalline structure, which allows a three-dimensional or two-dimensional ion conduction path to form. A notable example of this phenomenon is the room temperature stabilization of the superionic conductor α-Agl.1 Figure 1 shows the crystal structures of α-, β-, and γ-Agl. In α-Agl, the iodide ions form a body-centered cubic sublattice, and the silver ions move around between the iodide ions. A typical superionic conducting crystal, α-Agl, is a high-temperature phase that is only stable above 147°C.1 At a temperature lower than 147°C, it transitions to the low-conductivity β-Agl and γ-Agl phases. Figure 2 shows the temperature dependence of the conductivity for twin-roller quenched 90.1AgI·9.9Ag3BO3 (mol%).1 α-Agl has been reported to be stabilized even below 100°C by crystallization from glasses with a large amount of Agl.1 A series of glass-ceramics in the Li3S-based systems have also been discovered to be superionic conductors in the lithium family, and metastable phases of these glass-ceramics are formed from mechanochemically prepared sulfide glasses.14–16 Recently, we discovered a new but basic metastable phase: hexagonal Li3SnS6.17 Figure 3 shows the XRD patterns of Li3SnS6 samples prepared via a mechanochemical process. After a mechanochemical treatment, an amorphous sample was obtained. When the sample was heat-treated at 260°C, a novel phase with hexagonal structure was crystallized. Furthermore, in the sample heat-treated at 390°C, orthorhombic Li3SnS4, which is a stable phase, was obtained. Many materials with a high alkali metal content have high ion-binding properties. Such materials tend to have metastable crystalline phases in which cations

Figure 1. Crystal structure of polymorphs of AgI.

Figure 2. Temperature dependence of conductivity for the twin-roller quenched samples of 90.1AgI·9.9Ag3BO3 (mol%), in which α-Agl is the main crystalline phase, and for Agl crystal.
are randomly present in the interstices of the anion sublattices. When a mechanochemical treatment is performed on a crystal having a hexagonal close-packed anion sublattice, such as orthorhombic Li₄SnS₄, the anion forms a hexagonal close-packed sublattice similar to the stable phase, and cations randomly occupy one of the two tetrahedral sites that share a face. Some of the Li ions is believed to be widely distributed on the c-axis. This crystal structure can be represented as a simple structure in crystal model but there is significant variation in the local structure. As a result, a low crystalline material with poor long range order can be obtained.

Similarly, a sodium superionic conductor, metastable cubic Na₃PS₄ has been synthesized by crystallization of Na₃PS₄ glass.⁷ By a solid-phase reaction, tetragonal Na₃PS₄ is synthesized. On the other hand, when the glass prepared using the mechanochemical method is crystallized, metastable cubic Na₃PS₄ precipitates, and a sodium-ion conductivity of 4.6 × 10⁻⁴ S cm⁻¹, the highest conductivity in sulfide at the time it was reported, is obtained.⁸

4. Metastable Electrode Active Materials

The development of metastable materials is useful for electrode active materials because of high diffusion constant and a high symmetry. Here, Na₂TiS₃ is used as a representative example of a metastable material used as an electrode active material. Figure 4(a) shows the XRD patterns of Na₂TiS₃ compositions as electrode active materials for all-solid-state sodium secondary batteries. The samples were prepared using different mechanochemical treatment conditions in order to develop a novel crystal phase.
Treating a mixture of the starting materials mechanochemically at a rotation speed of 360 rpm yielded amorphous Na$_2$TiS$_3$. On the other hand, when the rotation speed was increased to 510 rpm, cation-disordered, cubic rock salt Na$_2$TiS$_3$ was obtained. Stable, monoclinic Na$_2$TiS$_3$, in which the cations (Na and Ti) are regularly arranged, is obtained by solid-phase synthesis; cubic Na$_2$TiS$_3$, on the other hand, is considered to be a metastable phase. The reversible capacities of amorphous Na$_2$TiS$_3$ and cubic Na$_2$TiS$_3$, both of which are metastable, were twice as large as those of the stable, monoclinic Na$_2$TiS$_3$. Substances having two kinds of cations that favor octahedral coordination tend to have a layered (or ordered) rock salt-analog structure as a stable phase. On the other hand, cation-disordered, cubic rock salt structure. This cation-disordered, cubic rock salt structure is usually a metastable phase. This is a general tendency also found in lithium-system such as Li$_2$TiS$_4$ and Li$_2$SnS$_3$ and oxide-based materials. The structure model is shown in Fig. 4(b) and (c).

5. Conclusions

This paper outlines our recent interests on battery materials made of metastable crystal phases and glass. We introduced representative crystal structures such cubic rock salt and hexagonal Li$_2$SnS$_4$ as metastable phases with cation disordering. Secondary batteries are an energy device that stores chemical energy by producing thermodynamically metastable materials. Metastable materials can be also utilized as the electrode active materials before charging and the solid electrolytes. The rapid quenching and mechanochemical processes are useful to obtain room temperature metastable materials. It is important to use the excellent physical properties that are generated by disordering the atomic arrangement. We hope that this paper will be a source of creative ideas for students and researchers involved in the development of metastable materials.

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