Status, issues and prospectives of lithium aluminates solid electrolyte including beta alumina in the form of film

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Abstract: Li-Beta alumina exhibited higher ionic conductivity than other lithium aluminate phases of LiAl₅O₈, LiAlO₂ and Li₅AlO₄ because of the special crystal structure having many conduction channels in c-plane. It is usually used as solid electrolyte in Battery. Compared with bulk and powder, Li-Beta alumina film takes advantages of decrease in area specific resistance, reduction of operating temperature, reduction of size/weight for battery and enhancement of battery cycle life. Laser chemical vapour deposition is used to achieve the first synthesis of Li-Beta alumina in form of film, which exhibits a high conductivity of 5.96 S∙m⁻¹∙K at room temperature. In this process, the remained issue of Li loss is essential to be fixed for large-scale production.

Keywords: electrical conductivity; beta alumina; crystal structure; film

1. Introduction

As people pay more attention to new energy technology, related metals and their compounds are extensively studied by researchers worldwide, such Li, Na, etc. The Li-Al-O system has several compounds of LiAl₅O₈, LiAlO₂ and Li₅AlO₄ and important Li-Beta alumina. Beta alumina exhibited very high ionic conductivity and is usually used as solid electrolyte in Battery, as depicted in Figure 1. Compared with Li₃N, LISICON and polymer-based lithium conductors, Li-Beta alumina has superior characteristic in ionic conduction.

Also LiAl₅O₈, LiAlO₂ and Li₅AlO₄ show more or less lithium ionic conductivity, which need more evidence to be applied to Li-battery so far. Of course they have lots of other properties of important. LiAl₂O₃ doped with rare-earth or transition ions is fine color emitting phosphors [1-3]. The dopant ions occupy tetrahedral sites in low-temperature α-phase or octahedral sites in high-temperature β-phase to produce emission spectra after excitation. LiAl₂O₃ (spinel) also has catalytic applications either as catalyst or as support because of excellent electron transfer ability, low surface acidity and higher catalytic activity than the traditional γ-Al₂O₃ support [4]. LiAlO₂ attracts increasing attention as a potential substrate for growing GaN semiconductor due to low lattice mismatch and removability [5]. It is also of interest as a solid tritium breeding material to produce tritium fuel by the nuclear reaction of Li (n, a)T in a fusion reactor, since LiAl₂O₃ shows high-temperature stability and good compatibility with structural materials under irradiation with neutrons [6]. Additionally, LiAl₂O₃ is thermochemically stable even at 973 K so that it is usually used as the support for the polymer electrolyte to form the diaphragm transporting CO₂ in molten carbonate fuel cells (MCFC) [7]. Aside from the stable LiAl₂O₃ and LiAlO₂, Li₃AlO₄ shows high reactivity with water (H₂O) and carbon dioxide (CO₂) in atmosphere because of high lithium content. Interaction between Li₃AlO₄ and H₂O causes the formation of LiOH, especially upon exposure to water vapor, which could lead to the humidity dependence of its conductivity. Therefore, Li₃AlO₄ is deemed to be a suitable material for humidity sensor [8,9]. Li₃AlO₄ also has high capacity of CO₂ absorption, which makes it a promising carbon dioxide captor [10]. For the amorphous Li-Al-O materials, ionic conduction was exhibited with low lithium content (Li/Al molar ratio less than 0.2).

For the application of them in Li-ion battery, the form of film takes advantages of decrease in area specific resistance, reduction of operating temperature, reduction of size/weight for battery and enhancement of battery cycle life, as shown in Figure 2. However, it is extremely difficult to synthesize their films due to high saturated vapor pressure of lithium. So it is necessary to discuss the current
situation, problem, and future development of these Li-ionic electrolyte films and attempt to find a solution, especially for Li-Beta alumina.

Figure 1: Schematic of Li-battery

Figure 2: Example of film battery

2. Preparation methods

Li-Al-O compounds in the forms of bulk and powder have been fabricated by solid state sintering, combustion and sol-gel methods. But only a few studies on the preparation of LiAl5O8 and amorphous lithium aluminate films were reported by using rf-magnetron sputtering, atomic layer deposition (ALD) and sol-gel methods. Significantly, there is no report on preparation of Li-Beta alumina film, which illustrates the complexity and difficulty for fabrication of lithium aluminate ceramics in the form of film. As we know, lots of processes, such as chemical vapor deposition (CVD), atomic layer deposition (ALD), physical vapor deposition (PLD) and tape casting (TP), can be used to achieve the preparation of various films including Li2O, Al2O3 and BaTi2O5, etc. Then, we try to use these methods to synthesize Li-Beta alumina film, resulting in no detection of Li in final products. This could be explained by the high crystalline temperature of Li-Beta alumina and high saturated vapor pressure of lithium at elevated temperature. Obviously, high temperature is a hinder for preparing lithium aluminate films including Beta alumina. Consequently, attempting to introduce laser or plasma to activate the reactants may decrease crystalline temperature of these films.

Laser chemical vapor deposition (laser CVD) is a deposition technique for films of various materials by introducing activated field with laser irradiation for chemical reaction. A cold-wall chamber was constructed as the main part of laser CVD setup. A continuous wave laser (Diode or YAG) was employed. Precursors were evaporated in the furnace and their vapors were transported to the reaction region (substrate) by Ar carrier gas. Before deposition, the substrate was preliminarily pre-heated and irradiated by the laser through a quartz window at an incident angle of 45°. The chemical reaction on the substrate surface was thus activated greatly, which decreased the preparation temperature and accelerated the deposition of films, as shown in Figure 3.

The parameters of deposition temperature ($T_{dep}$), laser power ($P_L$), molar ratio of Li/Al ($R_{Li/Al}$) and total pressure ($P_{tot}$) are mutually influenced in laser CVD. Figure 4 shows the effects of $P_L$ and $R_{Li/Al}$ on $T_{dep}$. The $T_{dep}$ linearly increased with increasing $P_L$ and decreased with increasing $R_{Li/Al}$. The increase of $R_{Li/Al}$ would have caused a rise in concentration of precursor vapors in chamber; thus more heat radiation could be accompanied at higher $R_{Li/Al}$, resulting in the decrease in $T_{dep}$.
Figure 4: Effects of $P_L$ (laser power) and $R_{Li/Al}$ (molar ratio of Li/Al) on $T_{dep}$ (deposition temperature).

Figure 5 shows the effects of $P_{tot}$ and $R_{Li/Al}$ on $T_{dep}$ at $P_L=150$ W. The $T_{dep}$ decreased with increasing $P_{tot}$ and $R_{Li/Al}$. At higher $P_{tot}$ or $R_{Li/Al}$, a higher concentration of precursors in gas phase existed in the chamber, causing more heat radiation from laser energy. That could lower the $T_{dep}$ in reaction area. With decreasing $P_{tot}$, the influence of $R_{Li/Al}$ on $T_{dep}$ became more notable.

Figure 5: Effects of $P_{tot}$ (total pressure) and $R_{Li/Al}$ (molar ratio of Li/Al) on $T_{dep}$ (deposition temperature).

Figure 6 shows the ratio $R_{Li/Al}$ as a function of $T_{Li}$ at $T_{Al} = 443$ K. The $R_{Li/Al}$ was estimated from the evaporated amounts of Al and Li precursors. By increasing $T_{Li}$ from 483 to 553 K, the $R_{Li/Al}$ approximately increased from 0.1 to 10.

Figure 6: Effect of $T_{Li}$ (evaporation temperature of Li precursor) on $R_{Li/Al}$ (molar ratio of Li/Al).

3. Crystal structures of Beta alumina and other lihitum aluminate compounds

Beta alumina group can be subdivided into those members containing a twofold screw axis in unit cell and those containing a threefold screw axis in unit cell. The archetypes of the two subgroups are designated $\beta$-alumina (twofold) and $\beta^\prime$-alumina (threefold), respectively. Both of Li-$\beta$-alumina and Li-$\beta^\prime$-alumina are characterized by structures composed of alternating slabs of closely-packed oxides (AlO$_4$, AlO$_6$) and loosely-packed layers with a low atom density containing mobile Li ions. Al$^{3+}$ cations
occupy both octahedral and tetrahedral interstices in the closely-packed slabs, forming a dense spinel block to prevent Li ions moving along c-axis. The loosely-packed layer supplies enough space for Li ions to move and is therefore named conduction plane. Li-β-alumina contains a mirror plane through the layer of mobile Li ions in the hexagonal unit cell, as shown in Figure 7.

Figure 7: Crystal structure of Li-β-alumina.

The crystal structure of α-LiAl5O8 is an inverse spinel with a cubic lattice (space group: P4332, lattice constant: a = 0.7908 nm), as shown in Figure 8 (a). The Li atoms and half of the Al atoms form six-coordinated octahedra sharing their edges. The other Al atoms form four-coordinated tetrahedra sharing corners of the octahedra. The phase of α-LiAl5O8 with a Li-poor and Al-rich composition is situated next to Li-β-alumina in the phase diagram of the Al2O3–Li2O system. Among the many polymorphs of alumina, γ-alumina has a defective spinel, as shown in Figure 8 (b) where Al atoms at tetrahedral and octahedral sites are designated as Al1 and Al2, respectively. The occupancy of the octahedral Al2 site is 0.83 to satisfy the Al2O3 stoichiometry in a spinel cubic cell. The crystal structure of α-LiAl5O8 can be understood as a derivative form of γ-Al2O3 with substitution of the Li-centered octahedra for a quarter of the Al2-centered ones.

Figure 8: Crystal structures of α-LiAl5O8 (a) and γ-alumina (b).

LiAlO2 has two types of structure, α: hexagonal caswellsilverite (NaCrS2)-type and γ: tetragonal wurtzite-type. γ-LiAlO2 has a wurtzite structure in a tetragonal cell (P41212; a = 0.517 nm and c = 0.6295 nm), which is composed of Al- and Li-centered tetrahedral, as shown in Figure 9. Each tetrahedron shares one of its edges with another tetrahedron of a different type, and each vertex of every tetrahedron is shared with two additional tetrahedra. The edge-sharing couples of Al- and Li-centered tetrahedra are aligned on (00l) planes. This directional alignment of the edge-sharing couples of tetrahedra could be associated with the preferred (001) orientation in the γ-LiAlO2 film.

Li5AlO4 also has two types of structure, α: antifluorite and β: antifluorite with greater disorder of the cations and vacancies in the tetrahedral sites. β-Li5AlO4 has a defective antifluorite structure (Pmmm; a = 0.642 nm, b = 0.6302 nm, and c = 0.462 nm), which is derivative form of the cubic antifluorite structure of Li2O. Figure 10 depicts schematics of the crystal structures of (a) β-Li5AlO4 and (b) Li2O. In the cubic antifluorite structure of Li2O, Li-centered tetrahedra with O atoms occupying the face-centered sites form an edge-sharing network. Compared with the crystal structures of Li2O shown in a different view in Figure 10 (c), the structure of β-Li5AlO4 is analogous to that of Li2O. The substitution of Al ions by Li ions at the center of the tetrahedra results in the formation of tetrahedral anion vacancies to satisfy charge compensation, accompanied by orthorhombic distortion from the cubic symmetry.
4. Electrical properties of Li-Al-O films

Figure 11: Comparison of electrical conductivities of α-LiAl5O8, γ-LiAlO2, and β-Li5AlO4 films.
The electrical conductivities of α-LiAl₅O₈, γ-LiAlO₂, and β-Li₅AlO₄ films were summarized in Figure 11. The dependence of logarithm of $\sigma T$ on inverse of temperature ($1000/T$) for Li-Al-O films showed a typical Arrhenius behavior. α-LiAl₅O₈ film almost had the same electrical conductivity as the reported data for its sintered sample. γ-LiAlO₂ film showed higher electrical conductivity than its sintered sample and α-LiAl₅O₈ film. β-Li₅AlO₄ film presented the highest electrical conductivity among the deposited Li-Al-O films, reaching 515 S·m⁻¹·K at 773 K. Although Li-rich film of Li₅AlO₄ exhibited very high ion conduction at high temperature, its electrical conductivity at room temperature is low and unable to replace Li-Beta alumina. Even at room temperature (298 K) Li-Beta alumina film has a $\sigma T$ value of 5.96 S·m⁻¹·K while it shows much higher lithium ion conductivity than other solid electrolytes at any prevailing temperatures. To date, the only problem to be solved for the application of Li-Beta alumina film electrolyte is saving the huge consumption of lithium-containing precursor, which is deemed to compensate the loss of Li at high synthesis temperature due to high vapor pressure of Li.

5. Conclusions

Lithium aluminate materials are used in numerous fields and their films exhibit superior characteristics, especially in electrical conduction. As solid electrolyte, Li-Beta alumina is the most suitable one of them due to loose channel of conduction c-plane in its crystal structure where lithium ions can move freely and rapidly. Furthermore, Li-Beta alumina in form of film can decrease resistance, reduce operating temperature and enhance battery cycle life. Although the preparation of Li-Beta alumina film is quite complex and difficult, laser or plasma used together with chemical vapor deposition process is able to pre-activate the gaseous precursor, which decrease synthesis temperature and avoid excessive loss of Li. In our previous work, laser-assisted CVD has been used to synthesize various ceramic films such as Al₂O₃ and CeO₂. Also laser CVD process is successful for preparation of Li-Beta alumina film, in which the remained issue we need to solve is saving raw materials. This could be accomplished throughout improvement of whole device and process optimization.

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References