Effect of Additive Concentrations on Sintering Behavior of the β''-alumina Solid Electrolyte

ผลของความเข้มข้นของสารเจือต่อพฤติกรรมการเผาผนึกของเบต้า-อลูมินาอิเล็กทรอไลท์ของแข็ง

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Abstract

Production of the ceramic β''-alumina solid electrolyte proposed for the electric vehicle battery system was a main aim of this work. A liquid phase sintering technique was employed to reduce the sintering temperature. Powder of β''-alumina with general formula $Na_{0.253}Mg_{0.747}Al_{10.253}O_{17}$ was synthesized by calcination at 1,250 °C for 10 hours. The XRD results indicate that calcination produced β''-alumina as the majority phase with a tiny amount of β'-alumina. Calcined powder was milled and mixed with 2 additives, $CaHPO_4$ and NTS glass ($2Na_2O.TiO_2.3SiO_2$) prior to shaping by the dry pressing technique. Two selected sintering temperatures were 1,075 and 1,400 °C. XRD results for the sample containing 15 mol% of $CaHPO_4$ and 15 mol% of NTS glass suggest that reaction of β''-alumina and the additives produced $AlNaSiO_4$ at 1,075 °C and $Na_2Si_2O_5$ at 1,400 °C. At higher concentration of $CaHPO_4$, the reaction produced $CaAl_2Si_2O_8$ with concentration proportional to the mol% of $CaHPO_4$. SEM study revealed larger grain sizes for the ceramic containing 20 mol% of $CaHPO_4$ and 10 mol% of NTS and sintered at 1,400 °C. It was also found that the density of the β''-alumina ceramics increased with increasing sintering temperature and the mol% of NTS glass.

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บทคัดย่อ

จุดมุ่งหมายหลักของงานวิจัยนี้มุ่งเน้นผลิตเซรามิกเบต้าอลูมินา (β''-alumina) ซึ่งเป็นอิเล็กทรอไลท์ของแข็งสำหรับระบบแบตเตอร์รี่ในรถไฟฟ้า โดยใช้เทคนิคการเจือสารให้อยู่ในสถานะของเหลวในขั้นการเผาผนึกเพื่อลดอุณหภูมิของการเผาผนึกลง ในการเตรียมผงเบต้าอลูมินาที่มีสูตรองค์ประกอบ $Na_{0.253}Mg_{0.747}Al_{10.253}O_{17}$ นี้สามารถเตรียมได้เมื่อผ่านการเผาแคลไซน์ที่อุณหภูมิ 1,250 องศาเซลเซียส ใช้ระยะเวลาเผาแช่นาน 10 ชั่วโมง ซึ่งยืนยันจากผลการตรวจวิเคราะห์ด้วยเทคนิค XRD ว่าเฟสหลักที่เกิดขึ้นเป็น β''-alumina ผงที่เตรียมได้ถูกนำไปผสมกับสารเจือ 2 ชนิดคือ $CaHPO_4$ และ แก้ว NTS ($2Na_2O.TiO_2.3SiO_2$) จากนั้นนำผงที่ได้ทำการขึ้นรูป อัดเม็ด และเผาซินเตอร์ที่อุณภูมิ 1,075 และ 1,400 องศาเซลเซียส เมื่อทำการตรวจวิเคราะห์ด้วยเทคนิค XRD พบว่า สารเจือทั้งสองปริมาณ 15 mol% ช่วยให้เฟส β''-alumina แน่นตัวขึ้นและเกิดปฏิกิริยากับสารเจือก่อเกิดเฟส $AlNaSiO_4$ เมื่อเผาซินเตอร์ที่อุณหภูมิ 1,075 องศาเซลเซียสและเฟส $Na_2Si_2O_5$ เมื่อผ่านการเผาซินเตอร์ที่อุณหภูมิ 1,400 องศาเซลเซียส เมื่อทำการเพิ่มความเข้มข้นของ $CaHPO_4$ ขึ้นพบว่าจะทำให้เกิดเฟสของ $CaAl_2Si_2O_8$ มากขึ้นด้วย จากภาพถ่าย SEM ของเซรามิกที่ผ่านการเผาซินเตอร์ที่อุณหภูมิ 1,400 องศาเซลเซียส เมื่อเจือด้วย $CaHPO_4$ 20 mol% และ NTS 10 mol% จะทำให้ได้เซรามิกที่มีเกรนขนาดใหญ่ และพบว่าเซรามิก β''-alumina ที่เตรียมได้มีค่าความหนาแน่นเพิ่มขึ้นเมื่อเพิ่มอุณหภูมิการเผาและปริมาณสารเจือ NTS

Keywords: β''-alumina solid electrolyte, liquid phase sintering, glassy additive, battery
คำสำคัญ: เบต้า-อลูมินาอิเล็กทรอไลท์ของแข็ง เผาผนึกด้วยเฟสของเหลว สารเจือ แบตเตอร์รี่

Introduction

To date, there have been several solid electrolytes employed in a variety of applications. β-alumina has become more interesting because it is promising for installation in the electric vehicle battery system which requires many special characteristics from the electrolyte. β-alumina shows conduction in 2D with special structure arrangement and its conductivity at ambient temperature is comparable to that of liquid electrolyte (Hench and West, 1990). This also has led β-alumina to be suitable for other kinds of applications such as gas sensors and fuel cells etc. In fact, "*β-alumina*" is a common name of the alkaline aluminate compounds with chemical formula denoted by $MAl_{11}O_7$ where M is a monovalent ion such as Na, K^+, Rb^+, Ag^+ or Li^+. β-alumina also has two other derivatives which are assigned as β'-alumina and β''-alumina with general formulae $M_{(1-x)}Al_7O_{11}$ and $M_{(1-x)}Al_5O_8$ (where $0<x<3$), respectively (Bruce, 1995). The monovalent M in these derivatives prefers to be Na^+ rather than other ions. At room temperature, β''-alumina exhibits the highest conductivity in this system. However, addition of MgO or Li_2O is required to stabilize β''-alumina and the corresponding composition becomes $Na_{1-x}Mg_{2x}Al_{5-x}O_8$ where x is essentially fixed at 0.175. During preparation, β''-alumina stability is the most important factor as it can transform to two other derivatives.

Using β''-alumina as the conductive layer in the electric car battery has been archived and the product has been named as the ZEBRA battery (Van

Zyl, 1996; Dustmann, 2004). However, readily dense MgO-stabilized β''-alumina prepared via conventional solid state sintering can be achieved only at high sintering temperature i.e. 1,700 °C. At this high sintering level, loss of Na content may also take place because of its volatility, leading to alteration of composition or sometimes involving phase change. Such high temperature sintering is also uneconomical and requires special instrumentation. Alternative methods have been employed to overcome this problem such as the sol-gel method (Jayaraman et al., 1998) and microwave sintering (Mathews et al., 2002; Subasri et al., 2003; Subasri, 2004) etc. But those methods require a complicated process as well as complex starting materials and yield only a small quantity of the product.

In this work, MgO-stabilized β''-alumina is prepared via the liquid phase sintering method. The aim is to study the sintering behaviour of MgO-stabilized β''-alumina with the presence of glassy additives which form a liquid state at the selected sintering temperature. The glass is selected to have composition close to $2Na_2O.TiO_2.3SiO_2$ (NTS glass). This glass composition exhibits highly ionic conduction with Na^+ as the mobile species. The glassy additive used in this work was prepared via the melt quenching method and its DTA profile is shown in Figure 1. Information from this DTA measurement revealed that the glass transition occurred at around 502 °C following by devitrification at 770 °C and melting above 1300 °C (Niyompan, 2002). The MgO-stabilized β''-alumina powder, which will be referred to as β'' for short throughout this work, was prepared using the conventional preparation route following by phase identification using the XRD technique. The effect of glass addition was studied in terms of densification, shrinkage and microstructure arrangement.

Material and Methods

The β'' ceramic powder was prepared using the conventional ceramics route with high purity reagent chemicals, i.e. MgO, Na_2CO_3 and α-Al_2O_3. The starting materials were weighed to the desired stoichiometry. Mixing was carried out using a ball mill with alumina media and acetone as the wetting agent. The mixed powder was calcined at 1250 °C for 10 hours with heating and cooling rates of 5 °C/min. During calcination, weight loss was also determined. The calcined powders were ground and identified using XRD and SEM techniques. Then, fine powders of NTS glass of the composition $2Na_2O.TiO_2.3SiO_2$ and $CaHPO_4$ were added and well mixed. The concentration of the additives was kept constant at 30 mol% but variation of $CaHPO_4$/NTS mol% ratio was applied. The appropriate quantity of poly-vinyl alcohol (PVA: 3 wt.%) was used as a binder prior to shaping by the dry pressing technique. The pellets were sintered at selected temperatures with a constant time of 4 hours. Phase identification was carried out again. The density of the ceramic pellets was determined using the Archimedes method and linear shrinkage was also measured. The microstructures of the ceramic samples were examined by scanning electron microscope.

Results and Discussion

Calcined Powder

The results of XRD investigation of the calcined powder shown in Figure 2 indicate that calcination of the mixture with β'' composition produced three identifiable phases. The β″ ($Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$) appeared as a major phase along with other two secondary phases, β′ ($Na_2MgAl_{10}O_{17}$) and $NaAl_{10}O_{17}$. This evidence suggests that the reaction between the three constituents did not produce pure powder but rather a mixture of several derivatives of the β-alumina family. This observation is also consistent with other reports (Van Zyl, 1996; Mathews, 2000), which suggest co-existence between β″ and β phases. In addition, the β″/β equilibrium has been found to be sensitive to composition and firing temperature (Näfe et al., 2000). Though the calcined powders do not present a single phase, the secondary phases are also in a category of high Na^+ ion conducting material which is a major requirement for the proposed application and should not have much effect on the electrical properties. The SEM micrograph of the calcined powder in Figure 3 demonstrates plate-like structure for β″, which is seen as packing of several layers with polygon shape, the same as in a previous report (Tulliani et al., 2004). There is also a variety of plate thickness but most of them do not exceed 1 mm. There is no obvious evidence of phase contrast according to SEM observation. All powder particles look the same. This is because all three phases found by XRD investigation have the same chemical constituents and only have slightly different structural arrangement.

Sintering of β″ Ceramics

The results of XRD investigation on the ceramics samples sintered at 1,075 °C are shown in Figure 4. There is no phase transformation observed for the β″ as their relative intensity compared to that of β′ remains almost unchanged. However, the presence of other phases is also observed resulting from the reaction between fractions of the β″ and two additives. A reaction with glassy additives gives the $AlNa(SiO_4)$ phase, while participation of $CaHPO_4$ in the reaction also gives $CaAl_2Si_2O_8$ as the product. Observed relative intensities of these two additional phases were not likely changed with modification of the additive concentration.

The XRD powder patterns of the ceramic samples sintered at 1,400 °C are illustrated in Figure 5. The same observations as for samples sintered at lower temperatures are found. But reaction between β″ and the additive gives only $CaAl_2Si_2O_3$. The additional phase is also detected and reflects the composition $Na_2Si_2O_5$. This phase may arise from the devitrification process of the glassy additive which is associated with the exothermic peak of its DTA trace shown in Figure 1.

The results of microstructural study are represented in Figure 6. Since the structure of β″ is built up from stacking spinel blocks (Reidinger, 1979), the microstructure arrangement is seen as packing of several plates with roughly hexagon shape. Hence, grain growth along the direction perpendicular to plate planes is more favored. This is the reason for the grain growth mechanism which is determined by diffusion jump and recrystallization procesess. At lower sintering temperature, 1,075 °C, development of several grains is clearly observed (Figure 6a) with variety of shape and size of approximately 1-3 μm. Grain boundaries are also visible. However, this grain development did not occur throughout the whole bulk of the samples. There is also porosity as the result of NTS glass contraction during the cooling process. This effect is more pronounced when the NTS glass concentration increases as shown in Figure 6b) in which larger pores are detected. At higher sintering temperature, 1,400 °C, higher shrinkage and densification can be seen but coarsening of the ceramic body is also found as the consequence of reaction between β″ and the additives.

The results of density measurement are summarized in Table 1. It can be seen that the density of β″ increases with increasing sintering temperature. At sintering temperature of 1,400 °C, the concentration of glassy additive also plays an important role in densification of the β″ as one containing higher glass concentration (1:1 of CP/NTS ratio) gives density value of 2.451 g/cm^3 compared to 2.080 g/cm^3 for one which contains lower glassy additive (5:1 of CP/NTS ratio). Densification may also be controlled by viscous flow of the NTS glass at high temperature. The present results prove that glass additive can induce a higher densification by forming a liquid state at the sintering temperature. However, contraction of glass can give rise to occurrence of porosity. This is because this glass composition may exhibit high viscosity at the sintering temperature. This clear result can be seen from porosity characteristics of the samples sintered at higher temperature in which larger pore size is found. This may indicate a higher degree of glass contraction at a higher sintering temperature.

There are several factors which have to be taken into account, in order to obtain the β″ ceramics with desired microstructure at considerably lower sintering temperature. As shown by the present results, concentration and type of the sintering aid plays an important part in microstructural control. A main difficulty is also from the characteristic of the β″ structure which has a 2D arrangement and layered structure which do not support a normal grain growth mechanism. Also, packing of those plates or sheets in 3D is a complicated process as the morphology of the calcined powders is seen as plate-like with reduced efficiency of initial powder packing (De Kroon et al., 2000). In order to get a better compact of the β″ powder particles, very fine particles may be required as well as a longer soaking time to allow a higher growth rate.

Conclusions

In summary, participation of the glassy additive plays an important role in the sintering behaviour of the β″-alumina ceramics. Higher glass concentration induces a higher degree of densification but also gives rise to larger pores as a result of the glass contraction. The $CaHPO_4$ additives tend to react with β″-alumina and give the calcium aluminosilicate phase as the product. Grain size also depends on additive concentration. The larger grain size was observed in the ceramic sintered at 1,400 °C with 20 mol% of $CaHPO_4$ and 10 mol% of NTS glass.

Acknowledgments

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Table 1. Density values of the β″-alumina ceramic.

Additive concentration ratio $CaHPO_4$/NTS glass	Apparent density from different sintering temperature (g/cm^3)	
	1,075 °C	**1,400 °C**
5:1	1.787	2.080
2:1	1.812	2.274
1:1	1.822	2.451

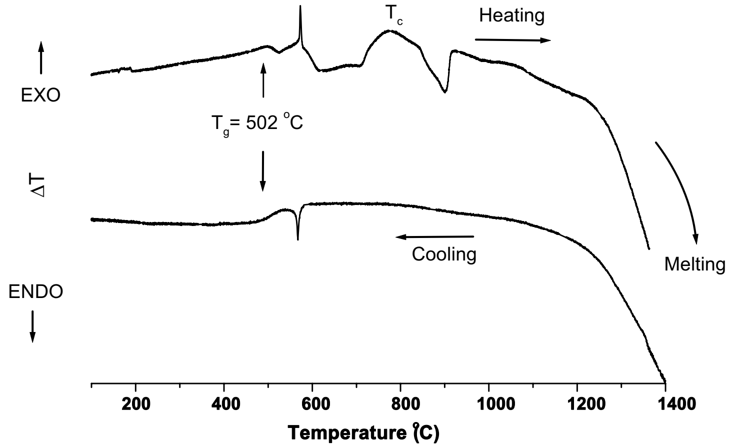

Figure 1. DTA traces of the glassy additive with composition $2Na_2O.TiO_2.3SiO_2$. Glass transition temperature (T_g) and crystallization peak (T_c) are illustrated.

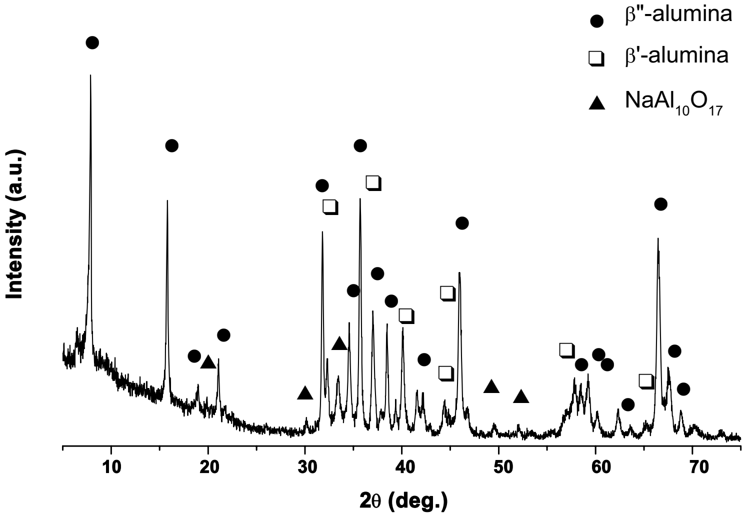

Figure 2. XRD powder pattern of calcined β″-alumina powder.

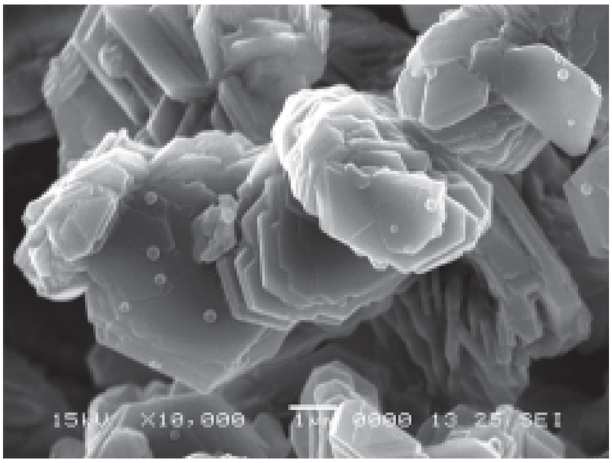

Figure 3. SEM micrograph of calcined powder.

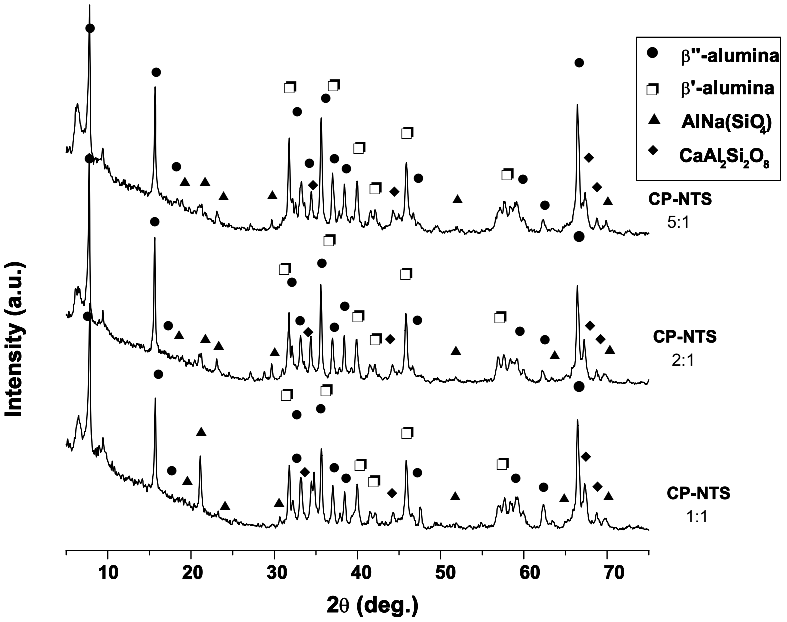

Figure 4. XRD powder patterns of the β″-alumina ceramics sintered at 1,075 °C with different additive concentrations. CP/NTS denotes the mol% ratio of CaHPO4 and NTS glass.

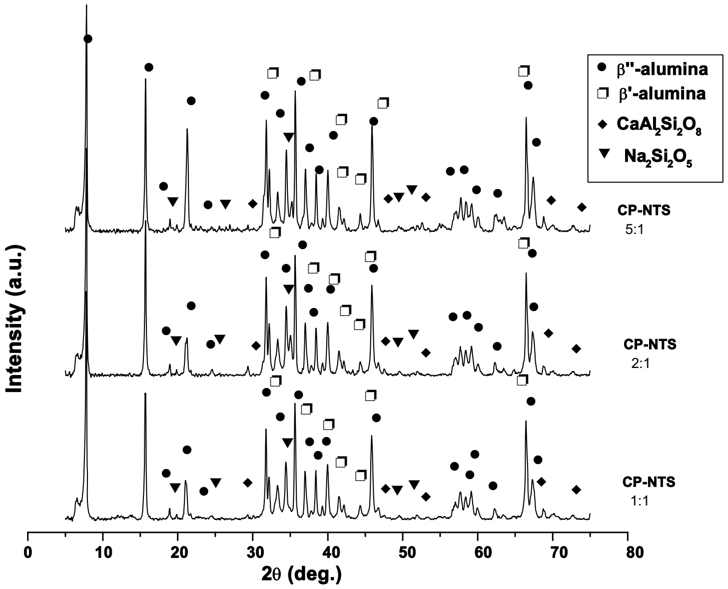

Figure 5. XRD powder patterns of β″-ceramics sintered at 1,400 °C with different additive concentrations. CP/NTS denotes the mol% ratio of $CaHPO_4$ and NTS glass.

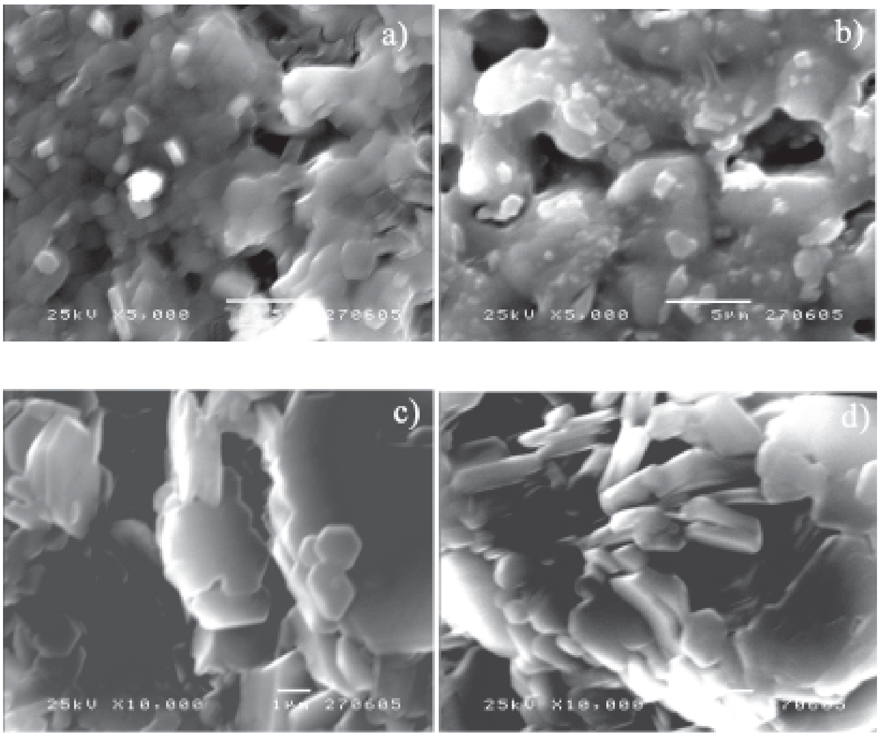

Figure 6. SEM micrographs of sintered pellet of β″ ceramic samples at 1,075 °C, a) and b) with CP-NTS of 2:1 and 1:1 respectively, and sintered at 1,400 °C, c) and d) with CP-NTS of 2:1 and 1:1, respectively.