Preparation of β"-Alumina Solid Electrolyte for Electric Car Battery

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Abstract

The MgO-stabilised β"-alumina ceramics with stoichiometry of Na\(_{1-x}\)Mg\(_x\)Al\(_{5-x}\)O\(_8\) (x = 0.175) were prepared via a liquid phase sintering technique with sodium ion conducting glass as a fluxing agent. The constituent oxides were calcined at appropriate temperature before addition of 5 mol% of glassy additive. Sintering process was carried out in the temperature range 1450-1550 °C. XRD results of calcined powder revealed that the β"-alumina present as a major phase with a small proportion of β’ alumina. There was also no phase transformation after increasing sintering temperature. Presence of glassy additive promotes porosity locally with precipitation of NaSiO\(_3\) crystals as the result of glass crystallization. Two-dimensional structural arrangement characteristic of the β"-alumina diminish its sinterability.

1. Introduction

MgO stabilized β"-alumina with corresponding composition Na\(_{1-x}\)Mg\(_x\)Al\(_{5-x}\)O\(_8\) (where x is essentially fixed at 0.175) is the most compromising candidate for electric car battery. This is because it has several advantages such as high ionic conductivity, high power density and environmental friendly. Commercial ZEBRA battery has been the great example of the real application [1, 2]. However, readily dense MgO-stabilized β"-alumina ceramics prepared via conventional solid state sintering can be achieved only with application of high sintering temperature i.e. 1700 °C. High temperature sintering is uneconomical and requires both special skill and equipment. Alternative methods have also been attempted to reduce sintering temperature such as Sol-Gel method [3] and microwave sintering [4-6] etc. But those methods require a complicated process as well as complex starting materials and yielding only a small quantity of the product.

In this work, MgO-stabilized β"-alumina was prepared using liquid phase sintering. The attempt is to study sintering behavior of the MgO-stabilized β"-alumina with presence of the glassy additive. The glass is selected from the Na\(_2\)O-ZrO\(_2\)-SiO\(_2\) system with a composition close to 2Na\(_2\)O.ZrO\(_2\).3SiO\(_2\). This glass composition exhibits highly ionic conduction with Na\(^+\) as the mobile species. The MgO-stabilized β"-alumina powder will be referred as β" for short throughout this work.

2. Experimental

The β" was prepared using conventional ceramics route with high purity reagent chemical, i.e. MgO, Na\(_2\)CO\(_3\) and Al\(_2\)O\(_3\). The starting materials were weighed to desired stoichiometry. Mixing was carried out using ball mill. The starting materials was calcined in an electric chamber furnace at two selected temperature, 1150 °C and 1250 °C, for 10 hr with heating rate and cooling rate of 5 °C/min. The calcined powders were ground and identified using XRD technique (Philips Xpert MPD). Glass of the composition 2Na\(_2\)O.ZrO\(_2\).3SiO\(_2\) was ground to fine powder with particles size < 36 µm prior to mixing process. A mixture the calcined powder and glass powder were well mixed in a mortar. Then ceramics pellets with diameter of 1.5 cm and 2 mm thick were formed using dry pressing technique. The pellets were sintered at three different selected temperatures, 1450, 1500 and 1550 °C with a constant time of 4 hr. Phase identification was carried out again. Densities of ceramic pellets were determined using Archimedes’ method. Microstructure of the ceramic
samples were examined by scanning electron microscope (JEOL JSM-840A).

3. Results and discussion

3.1 Phase identification

The XRD results of calcined powders are shown in Fig.1a. At the lower calcination temperature, 1150 °C, reaction between three constituent oxides gave two equilibrium phases, i.e. \( \beta'' \)-alumina and \( \beta' \)-alumina.

![XRD powder patterns of \( \beta'' \)-alumina calcined at different temperatures](image)

**Figure 1** XRD powder patterns of \( \beta'' \)-alumina calcined at different temperatures. \( \square \) = \( \beta'' \)-alumina, \( \bullet \) = \( \beta' \)-alumina, \( \text{O} \) = \( \text{Al}_2\text{O}_3 \), \( \text{D} \) = \( \text{MgO} \) and \( \text{\text{\text{\n}}} \) = \( \text{Na}_2\text{CO}_3 \), respectively.

The intensity of the patterns reveals that the \( \beta'' \) present as a main phase. For calcination at 1250 °C, \( \beta' \)-alumina still be present but with only small concentration. These results reveal that both the \( \beta' \) and \( \beta'' \) phases always co-exist in this particular system. The same co-existence has been already reported and studied theoretically in term of the \( \beta'/\beta'' \) equilibrium by Maass et al [7]. From the experimental point of view, the \( \beta'/\beta'' \) equilibrium has been found to sensitive to phase composition and firing temperature [8]. Fig. 1b shows the XRD results of the crushed pellets after sintering at several temperatures.

With comparison to Fig. 2a, it is clearly seen that there is no phase change after sintering. There is no clear evidence of temperature dependence of the \( \beta'/\beta'' \) equilibrium as the relative intensities of these two phases do not change with temperature.

3.2 Apparent Density

**Table 1** shows apparent density values of the \( \beta'' \)-alumina ceramics.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sintering Temp. (°C)</th>
<th>Apparent Density (g/cm²)</th>
</tr>
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<tbody>
<tr>
<td>B1</td>
<td>1450</td>
<td>2.591</td>
</tr>
<tr>
<td>B2</td>
<td>1500</td>
<td>2.692</td>
</tr>
<tr>
<td>B3</td>
<td>1550</td>
<td>2.897</td>
</tr>
</tbody>
</table>

From Table 1, It can be seen that density of the \( \beta'' \) alumina ceramic samples increase with increasing sintering temperature. The value of 2.897 g/cm² of the sample sintered at 1550 °C is about 88 % of the theoretical value.

3.2 Microstructural investigation

In Fig. 2a, It can be seen that the \( \beta'' \)-alumina powder particles are clearly built up from the packing of several plates. This characteristic is a typical layered structural arrangement of the \( \beta'' \)-alumina, which each layer consists of stacks of the spinel-like blocks [9, 10]. There is a variety of the plate thickness. Fig 2b shows SEM micrograph of the sintered samples. At the surface, high porosity is clearly seen for all samples. The crystals with needle-like shape are NaSiO₃. These impurity crystals are the product of crystallization process in the glassy additive. This observation demonstrates that NaSiO₃ prefers a surface crystallization as reported previously [11].

It can be seen that as the sintering temperature was increased, higher densification was observed as evidenced by the density values of the bulk samples from Table 1. However, large pores are clearly seen in the samples sintered at 1450 and 1500 °C. Observation of those pores also associates with detection of the NaSiO₃...
crystal cluster around the pore sites. Thus, this result may show that devitrification of the glassy additive during cooling process induces a relatively large pore. It is no clear explanation for the mechanism of this porosity. There may be three possible major responses: 1) the difference of thermal contraction between $\beta''$ and NaSiO$_3$, 2) volatile nature of the residual glass at high temperature which its loss can promote a large pore or 3) viscous flow of the glassy additive. Thus, from the present study it has been found that selection of an appropriate glass composition is very important. The glassy additive should exhibit a lower degree of crystallization. Concentration of the glass and mixing condition are also important. The major difficulty of $\beta''$ densification is two-dimensional characteristic of their crystal structure. Morphology of the calcined powders is plate-like shape which can reduce the efficiency of the initial powder packing. This behavior has been also reported for the $\beta'$ phase [12].

**Figure 2** a) SEM micrograph of $\beta''$-alumina powder calcined at 1250 °C and b)-d) SEM micrographs of surface of the $\beta''$-alumina ceramics sintered at 1450, 1500 and 1550 °C, respectively.

The major concern of $\beta''$-alumina production for use in car battery is to obtain a high mechanical strength ceramic couple with high ionic conduction ($\sigma > 10^{-3}$ S/cm). Thus, it is sensible to get a desirable ceramics with an appropriate microstructure before further investigations in area of electrical properties. From the present study, the $\beta''$-ceramic samples show some degree of sinterability at lower temperature but their densification are not high enough as this would lower the ionic conductivity by the effect of large grain boundary and pore.

4. Conclusion
The present study has demonstrated that calcination of MgO-stabilized $\beta''$-alumina gives a mixture of $\beta'$ and $\beta''$ phases. Introduction of glass powder with composition 3Na$_2$O.ZrO$_2$.3SiO$_2$ during sintering promotes NaSiO$_3$ with needle-like crystal as the consequence of devitrification process of the glass. This glass composition does not enhance sinterability of the $\beta''$ but rather induce the presence of porosity. Two-dimensional structural arrangement is also responsible for low sinterability of the $\beta''$.

**References**