Structure and properties relationships of beta-Al$_2$O$_3$ electrolyte materials

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ABSTRACT

Beta-Al$_2$O$_3$ electrolyte materials were synthesized by solid-state reaction method in this paper. The effect of different stabilizers on the β″-phase content of the beta-Al$_2$O$_3$ electrolyte and the structures of aluminum-oxide polyhedron were investigated by X-ray diffraction technology (XRD) and ^{27}Al MAS NMR, and the relationship between the β″ phase content and the amounts ratio of octahedron and tetrahedron ($A_{Al(VI)}/A_{Al(IV)}$) was summarized. The results showed that the β″ phase was stable at high temperatures and the β″ phase content increased with the temperature increasing by the addition of the stabilizers. Meanwhile, $δ_{Al(IV)}$ and $δ_{Al(VI)}$ moved towards down field, and $A_{Al(VI)}/A_{Al(IV)}$ decreased with the β″ phase content increasing. The Mg^{2+} stabilizer was better to improve the symmetry of Al(VI) than the Li$^+$ stabilizer.

1. Introduction

The polycrystalline beta-Al$_2$O$_3$, one of the well-known solid electrolyte materials used in sodium–sulfur batteries and sodium–nickel chloride batteries [1,2], is normally a non-stoichiometric compound and has two similar crystalline phases of β″- and β-phases [3]. The β″-phases are more desirable since it has 3–4 times higher ionic conductivity than that of β-phase. Therefore, the different structures of beta-Al$_2$O$_3$ have a significant effect on its performance. In published works preference is generally given to the β″-Al$_2$O$_3$ phase stabilized with Li$^+$, Mg^{2+} or with a mixture of these two oxides [4,5]. And the approximate relative amounts of β″ and β-phases are appreciated from their own characteristic diffraction peaks respectively. However, few researches had been done in terms of the effect of the stabilizers on the aluminum-oxide polyhedron structure and the relationship between the relative content of two phases of the aluminum-oxide polyhedron structure. The technique of ^{27}Al magic-angle spinning (MAS) NMR spectroscopy has become an important research and analytical tool in the characterization of a variety of polycrystalline and amorphous materials since its invention in 1945 [6]. In the recent report of Chen et al. [7], the coordination states of aluminum species in calcined HZSM-5 zeolites had been investigated using ^{27}Al MAS and 2D MQMAS methods. Wang et al. [8,9] studied the aluminum-oxide stereo polyhedron structures by ^{27}Al MAS NMR and SEM in fly ashes treated

by mechanical grinding. The present work was conducted in order to discuss the effect of stabilizers and phase composition on the aluminum-oxide polyhedron structure. This made a theoretical basis for the preparation of beta-Al$_2$O$_3$.

2. Experimental

Beta-Al$_2$O$_3$ was fabricated from powder mixtures of high-purity α-Al$_2$O$_3$, reagent-grade Na$_2$C$_2$O$_4$, Li$_2$CO$_3$, Mg(OH)$_2$, and the compositions. And mass ration for this study were summarized in Table 1. The additives, such as LiAl$_5$O$_8$, Li$_2$CO$_3$ and Mg(OH)$_2$, were utilized as the stabilizing sources of beta-Al$_2$O$_3$. The stabilizer LiAl$_5$O$_8$ was prepared by mixing appropriate amounts of dried Li$_2$CO$_3$, α-Al$_2$O$_3$ and calcining the mixture at 1523 K for 2 h. The pure LiAl$_5$O$_8$ was detected in the resulting powder by X-ray diffraction. The 1#–5# compositions in Table 1 were ball-milled with ethanol for 10 h and dried at 353 K, then calcined at 1573 K for 2 h. These products were the precursor powders of beta-Al$_2$O$_3$. The Na$_2$O·5Al$_2$O$_3$ was the precursor powder without any stabilizer. The precursor powders were ball-milled with ethanol for another 10 h and then dried. Some polyvinyl alcohol was added as a binder. Pellet specimens with a diameter of 20 mm were uniaxially pressed at about 100 MPa and then isostatically pressed at 300 MPa. The green ceramics were covered with powders of the same compositions and fired at 1873 K for several minutes. Meanwhile, the stabilizing effect of LiAl$_5$O$_8$ and Li$_2$CO$_3$ respectively on Na$_2$O·5Al$_2$O$_3$ were also investigated, which can be seen from 6# and 7# compositions in Table 1.

The phase composition analysis of the precursor powders and sinters was carried out on the Dmax/rB X diffraction analyzer using CuKα radiation over the range of 5–80° (2θ). The scanning speed of the gonimeter was 5° (2θ) per minute. Solid-state ^{27}Al MAS NMR experiments of the precursor powders and sinters were performed at a resonance frequency of 104.26 MHz using a high magnetic field (9.4 T) on a Bruker AVANCE-400 spectrometer at room temperature. The delay time was 0.5 s and spinning rate was 8 kHz. The relative amounts of Al(IV) ($A_{Al(IV)}$) and Al(VI) ($A_{Al(VI)}$) were calculated from the area intensity ration of the peaks corresponding to Al(IV) and Al(VI), respectively. The sinter samples for the test of NMR were crushed and passed through 270 mesh sieve.

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Table 1
Compositions of beta-Al_2O_3 solid electrolyte.

No.	1#	2#	3#	4#	5#	6#	7#
Starting materials	$Na_2C_2O_4Al_2O_3$	$Na_2C_2O_4Al_2O_3$	$Na_2C_2O_4Al_2O_3$	$Na_2C_2O_4Al_2O_3$	$Na_2C_2O_4$ Al_2O_3	$Na_2O·5Al_2O_3$	$Na_2O·5Al_2O_3$
Stabilizer	–	$LiAl_5O_8$	Li_2CO_3	$Mg(OH)_2$	$LiAl_5O_8Mg(OH)_2$	$LiAl_5O_8$	Li_2CO_3
Composition content, wt%							
Na_2O	10.84	9.50	9.50	9.50	9.50	9.50	9.50
Li_2O	–	0.70	0.70	–	0.70	0.70	0.70
MgO	–	–	–	5.0	2.00	–	–
Al_2O_3	89.16	89.80	89.80	89.80	87.80	89.80	89.80

3. Results and discussion

3.1. XRD and ^{27}Al MAS NMR spectroscopy analysis of the precursor powders

It was shown in Fig. 1 that all samples contained β"- and β-phases in different calcinations at 1573 K. Since β"- and β-phases have similar X-ray diffraction peaks, the relative amounts of β"- and β-Al_2O_3 in each sample were determined from the integrated intensities of the (0 1 7) β- and (0 1 1 1) β"-diffraction peaks using the method described by Youngblood et al. [10]. As can be seen from Fig. 1, the neighboring peaks occurred at 33.4° and 34.6° of 2θ, respectively. So the relative amounts of β"-phase of the 1#–5# precursor powders were 81 wt%, 68 wt%, 56 wt%, 59 wt% and 62 wt%, respectively. This indicated that $LiAl_5O_8$-stabilized system could produce more β"-phase in comparison with the Li_2CO_3-stabilized compositions. It had been reported that $LiAl_5O_8$ had more volume than Li_2CO_3 [11], therefore $LiAl_5O_8$ could induce more uniform distribution of Li^+ ions and increase the fractions of β"-phase during the preparation process. Obviously, the stabilization effect in the $LiAl_5O_8$-$Mg(OH)_2$-stabilized system was better than that of the $Mg(OH)_2$-stabilzed system, but worse than that of the $LiAl_5O_8$-stabilzed system. In comparison with the $Na_2O·5Al_2O_3$ powder, no more β"-phase fractions had been formed in the stabilized system. It was considered that the effect of stabilizers on the β"-phase formation would occur at the higher temperature.

The β" and β-phases in beta-Al_2O_3 have basically close packed structures with 2 and 3 spinel blocks [12], respectively. And the arrangement of Al^{3+} and O^{2-} ions in the unit crystals of β" and β-phases is same as that of $MgAl_2O_4$ [13]. Generally, the tetrahedron coordinating aluminum structure (Al(IV)) has a high chemical shift, while the octahedron coordinating aluminum structure (Al(VI)) has a low chemical shift [14]. It was shown that beta-Al_2O_3 had a peak at 50 ppm assigned to Al(IV) and a peak at −6 ppm assigned to Al(VI) in Fig. 2. Since both β" and β-phases existed in the precursor powders, the ^{27}Al MAS NMR spectra of precursor powders
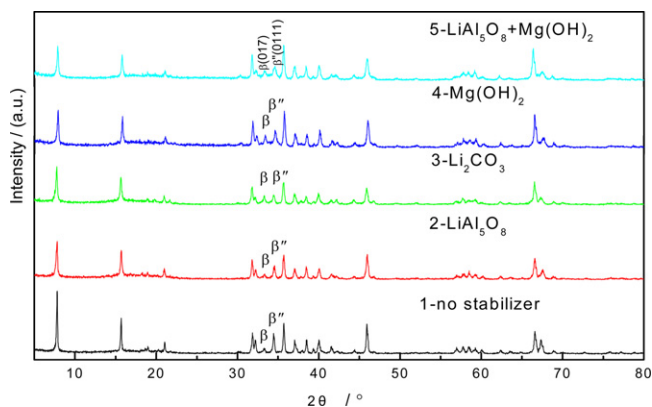
Fig. 1. XRD patterns of precursor powders with different stabilizers.
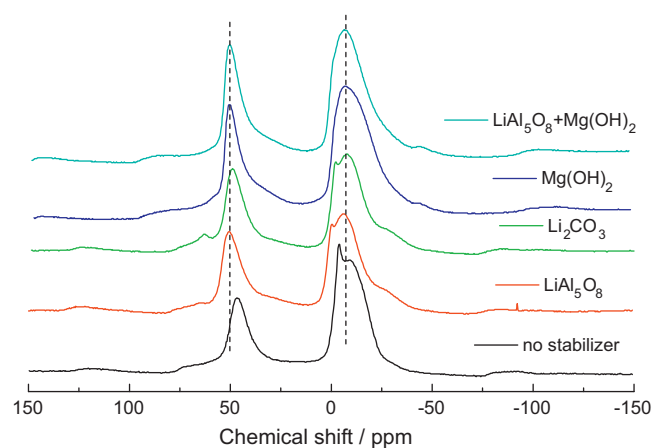
Fig. 2. ^{27}Al MAS NMR spectra of precursor powders with different stabilizers.

displayed asymmetrical signals and the widening of the Al(IV) and Al(VI) peaks, especially the obvious division of Al(VI) spectra. In comparison with the $Na_2O·5Al_2O_3$ powder, the symmetry of Al(VI) peaks was improved in the precursor powders stabilized with the $LiAl_5O_8$ and Li_2CO_3 respectively. In the Mg^{2+}-stabilized system and Mg^{2+}-Li^+-stabilized system, the peaks of Al(IV) and Al(VI) became more pronounced and the division of the Al(VI) peaks mostly disappeared. It was demonstrated that the Mg^{2+} stabilizer was more beneficial to the environmental improvement of the aluminum-oxide polyhedron structure than the Li^+ stabilizer, which was in good agreement with the uniform microstructure in beta-Al_2O_3 stabilized with Mg^{2+} ionic.

Table 2 presented the chemical shift of Al(IV) ($\delta_{Al(IV)}$), Al(VI) ($\delta_{Al(VI)}$), the amounts ratio of Al(IV), Al(VI) ($A_{Al(VI)}/A_{Al(IV)}$) in different precursor powders. It was found that in comparison with $Na_2O·5Al_2O_3$, $\delta_{Al(IV)}$ and $\delta_{Al(VI)}$ of precursor powders with stabilizers moved towards down field obviously. It can be explained properly by the decrease of Al extranuclear electron density from the substitution effect of stabilizers. As shown in Table 2, $A_{Al(VI)}/A_{Al(IV)}$ in the 1# precursor powder was larger than that in the 2#, 3#, but smaller than that in 4#, 5#. In comparison with the ideal composition of β"-Al_2O_3 [15], the compositions of beta-Al_2O_3 in this experiment had extra Na^+ ions. Stabilization of β"-phase was basically the substitution of Al^{3+} ions by the cations of stabilizers to

Table 2
The chemical shift of the Al–O structure of the precursor powders.

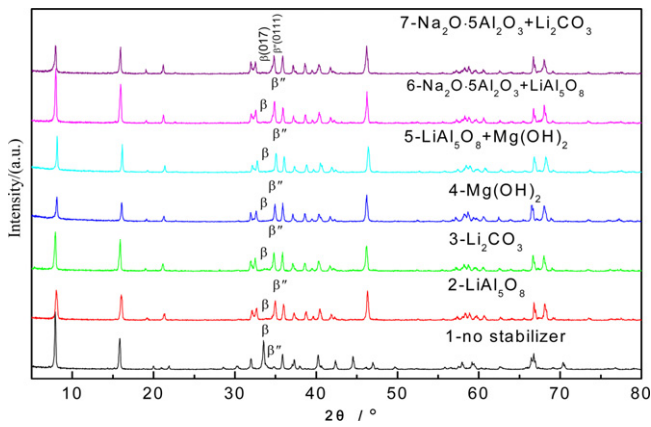| Al–ONo.	$\delta_{Al(IV)}$ (ppm)	$\delta_{Al(VI)}$ (ppm)	$A_{Al(VI)}/A_{Al(IV)}$	β" phase content (wt%)
1#	46.7	−9.1	1.74	81
2#	51.1	−6.7	1.48	68
3#	48.9	−6.2	1.54	56
4#	50.1	−6.5	1.87	59
5#	50.4	−6.5	1.83	62

Fig. 3. XRD patterns of sinters with different stabilizers.

compensate extra Na^+ ions. It had been reported that the compensating Li^+ ions generally substituted the octahedral Al^{3+} ions, and Mg^{2+} ions substituted tetrahedral Al^{3+} in the spinel blocks [11]. Hence, the $A_{Al(VI)}/A_{Al(IV)}$ decreased in the Li^+-stabilized system, but increased a little in the Mg^{2+}-stabilized system.

3.2. XRD and ^{27}Al MAS NMR spectroscopy analysis of the sinters

Fig. 3 presented XRD patterns of sinters manufactured by different technologies. It was found that the characteristic peak of β-phase was particularly obvious in the 1# sinter, and the β''-phase fractions were only 5 wt%, which were much smaller than that in the 1# precursor powder. But in the 2#–7# sinters, the characteristic peak of β-phase was very weak, the β''-phase fractions were up to 93 wt%, 88 wt%, 91 wt%, 96 wt%, 98 wt%, 98 wt%. As expected, the β''-phase fractions of the sinters were much more than that of the precursor powders, and the sinters with more pure β''-phase were easily obtained in the precursors containing more β''-phase fractions. Moreover, the formation of β''-phase occurred more easily in the materials with the double stabilizers than that with single stabilizer.

According to the XRD patterns of 1#, 6#, and 7# sinters, the transformation of β'' to β-phase was held effectively back by the addition of stabilizers. In addition, the formation of β'' phase could be easier by adding stabilizers in $Na_2O·5Al_2O_3$ than adding stabilizers directly in the starting materials.

Fig. 4 showed ^{27}Al MAS NMR spectra of beta-Al_2O_3 sinters. An unknown peak occurred at 62 ppm in the 1# sinters, which was considered to be related to the high β phase fractions. In β-Al_2O_3 crystals, Al^{3+} ions left the original equilibrium position to become the interval Al^{3+} ions in the conducting plane layer due to the extra Na^+ ions, and the interval O^{2-} ions of the crystal structure provided the tetrahedral coordination for Al^{3+} ions and compensated the extra Na^+ ions [16]. Therefore, a new Al(IV) spectrum occurred in the sinter when the β phase became the major phase. Compared to the 1# sinter, $\delta_{Al(IV)}$ and $\delta_{Al(VI)}$ in different sinters with stabilizers moved towards down field. But the migration rate in the sinters was smaller than that in the precursor powders. It was considered that $\delta_{Al(IV)}$ and $\delta_{Al(VI)}$ in the sinters became close to each other due to the uniform of beta-Al_2O_3 with the temperature increasing.

As can be found in Fig. 4, in comparison with the $Na_2O·5Al_2O_3$ sinter, the symmetry of Al(VI) peaks was improved in the sinters stabilized with $LiAl_5O_8$ and Li_2CO_3 respectively. In the 3# and 4# sinters, the peaks of Al(IV) and Al(VI) became more pronounced and the division of the Al(VI) peaks mostly disappeared. It was demonstrated that the Mg^{2+} stabilizer was beneficial to the environmental improvement to the aluminum-oxide polyhedron structure. Table 3 showed that the $A_{Al(VI)}/A_{Al(IV)}$ of sinters further decreased in
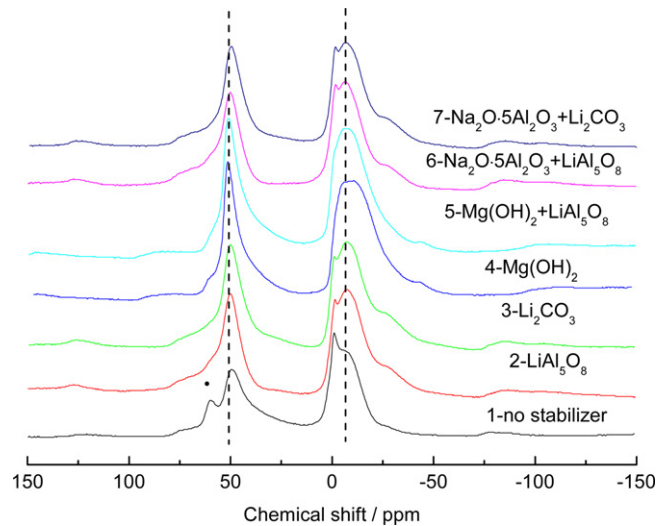

Fig. 4. ^{27}Al MAS NMR spectra of beta-Al_2O_3 sinters with different stabilizers.

Table 3
The chemical shift of the Al–O structure of the sinters.

Al–ONo.	$\delta_{Al(IV)}$ (ppm)	$\delta_{Al(VI)}$ (ppm)	$A_{Al(VI)}/A_{Al(IV)}$	β'' phase content (wt%)
1#	49.1	−7.0	1.10	5
2#	50.2	−6.6	1.32	93
3#	49.9	−6.8	1.39	88
4#	51.3	−6.5	1.62	91
5#	51.2	−6.7	1.48	96
6#	50.1	−6.6	1.28	98
7#	49.5	−6.8	1.28	98

comparison with the precursor powders, and the intensity of Al(IV) spectra was strengthened clearly. It can be concluded that the decrease of the $A_{Al(VI)}/A_{Al(IV)}$ was resulted from the transformation of β phase to β'' phase according to the change of the β'' phase fractions both in precursor powders and sinters.

According to Tables 2 and 3, the relationship between the β'' phase fractions and the $A_{Al(VI)}/A_{Al(IV)}$ was shown in Fig. 5 in Li^+-stabilized and Mg^{2+}-stabilied systems, respectively. It was obvious that the $A_{Al(VI)}/A_{Al(IV)}$ gradually decreased with the increase of the β'' phase fractions after adding the stabilizers, and the two parameters displayed the linear relationship in these two different systems. Therefore, the β'' phase fractions in the Li^+-stabilized or
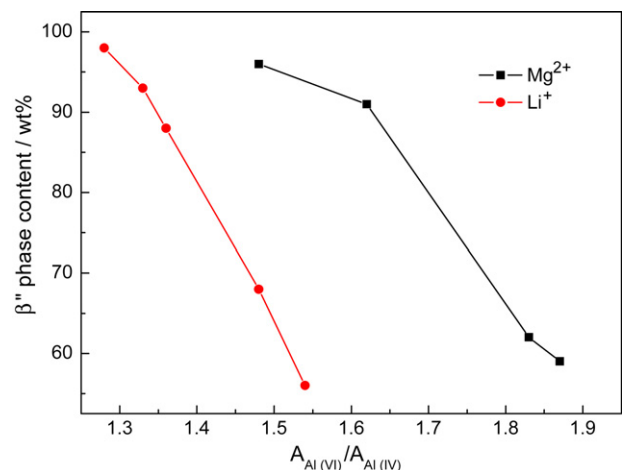

Fig. 5. The value of $A_{Al(VI)}/A_{Al(IV)}$ vs. β'' phase content.

Mg^{2+}-stabilized system can be deduced from the $A_{Al(VI)}/A_{Al(IV)}$. It provided a new calculation method for the β" phase fractions.

4. Conclusions

(1) The β" phase of beta-Al_2O_3 was stable in high temperature and the β" phase content increased with the sintering temperature rising by the addition of the stabilizers.

(2) $\delta_{Al(VI)}$ and $\delta_{Al(IV)}$ of beta-Al_2O_3 moved towards down field in different systems with different stabilizers. Li^+ and Mg^{2+} ions substituted the octahedron and tetrahedral Al^{3+} ions in the spinel blocks respectively, and Mg^{2+} stabilizer was more benefit to improve the symmetry of Al(VI) of the beta-Al_2O_3 than Li^+ stabilizer.

(3) The amounts ratio of octahedron and tetrahedron ($A_{Al(VI)}/A_{Al(IV)}$) of beta-Al_2O_3 decreased with the β" phase content increasing.

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