Development of ceramics of Na-β-alumina and Na-β-alumina/TZ3Y for eletrochemical applications

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Abstract

The solid electrolyte Na-β-alumina has a differentiated crystalline structure that allows great mobility of sodium ions. The ceramics were sintered in two-step sintered from the mixing and milling of oxides. This study to develop Na-β-alumina and Na-β-alumina/TZ3Y ceramic composite with the purpose of improving densification. To evaluate the electrical performance, it was possible to calculate the electrical conductivity of Na-β-alumina based on the analysis of impedance spectroscopy data.
Keywords: solid electrolyte, β-alumina batteries, two-step sintering.

Introduction

Beta-alumina (Na-β-alumina) ceramics have na unusual crystalline structure that allows high mobility of sodium ions. The crystalline structures differ in chemical stoichiometry, stacking and oxygen ion sequence across the conduction plane. Due to this difference in the oxygen stacking sequence, the β´´-alumina unit cell is 50% larger than that of β-alumina, thus presenting a higher sodium ion conductivity[1].

The main objective of the presente work is to obtain the solid electrolyte Na-β-alumina and the ceramic composite Na-β-alumina/TZ3Y using powders prepared by the oxide mixing and grinding process in two-step sintering ant to evaluate its electrical performance. Na-β-alumina presentes low sinterability the addition of stabilized zircônia with 3%mol of yttria (TZ3Y) caused a decrease in the initial shrinkage temperature and the impedance spectroscopy technique was importante in the electrical conductivity calculation.

Experimental Procedure

Nominal composition powders 8,5%Na_2CO_3.1%$Mg(OH)_2$.90,5%Al_2O_3 (wt%) were obtained by mixing sodium carbonate (Synth 99,5%) and alumina oxide (Alcoa 99,5%). The reagents were then mixed with isopropyl alcohol in a zirconia jar containing spheres of the same material as milling elements filling in the 1:3 ratio of the jar. After milling (Frizstch Pulverisette 4(for 8 hours, the suspension was dired under air flow (T~60°C) and the powder was granulated in 80 mesh (150µm) sieve. Then the powder was calcined in lined alumina crucibles at 1200°C for 2 hours. Subsequently, a new composition 10,5% Na_2CO_3.1%$Mg(OH)_2$.88,5%Al_2O_3 (%wt) was prepared and calcined at 1200°C for 2 hours.

Subsequently, the above process was repeated, with powders of nominal composition 95%β-Al_2O_3.5% TZ3Y, 85%β-Al_2O_3.15% TZ3Y e 75%β-Al_2O_3.25%TZ3Y (%wt). β-alumina (previously obtained and Ytria stabilized Zirconia (Tosoh-Japan). The resulting powders were formed into cylinders (d_0=6mm and L_0=10mm) in a metal mold. The specimens were encapsulated under vacuum in a suitable plastic packaging and were isostatically pressed at 200MPa for 1

minute using the AIP CP 360 isostatic press. Two-step sintering of the eletrolytes was performaded at 1600°C for 20 minutes and 1475°C for 2 hours in the Lindberg oven Blue-M model.

To obtain the β phase, the powders were analyzed by X-ray diffraction. The sintered samples were characterized by the following techniques: measurement of green density and sintered body density, dilatometry, X-ray diffraction and electrical conductivity measurements.

Electrical characterization was performed by impedance spectroscopy (EI) analyzes were performed on the sample coupled between two stainledd steel plates. Impedance was measured with alternating current in the frequency rang 10MHz to 1Hz, 500mV oscillating voltage using an impedance meter (Solartron SI 1260/Gain-Phase Analyzer).

Results and Discussion

Figure 1 shows the X-ray diffractograms of Na-β-alumina samples and the sintered Na-β-alumina/TZ3Y ceramic composite at 1600°C/20minutes and 1475°C for 2h. It is noted that a phase mixture (β/β´´) was formed as expected in the 100β sample and in the samples with diferente zirconium concentrations the formation of the β-alumina phase occured.

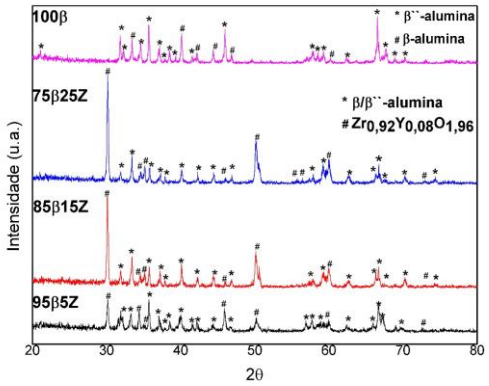
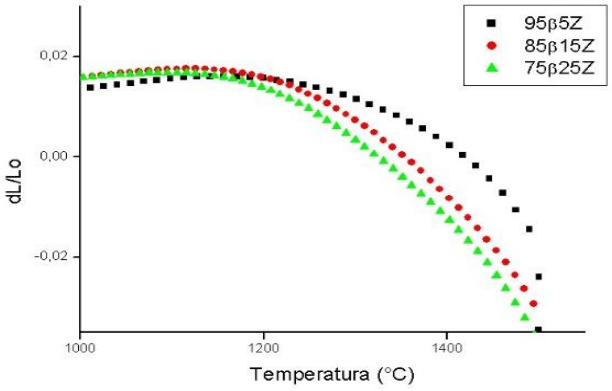


Figure 1: X-ray diffractograms of Na-β-alumina and Na-β-alumina/TZ3Y (75β25Z, 85β15Z and 95β5Z).

Figure 2 shows the linear shrinkage values of all Na-β-alumina/TZ3Y and Na-β-alumina composition nomoinal and modified composition respectively. It can be seen Figure 2.a that the presence of ytria stabilized zircônia (TZ3Y) caused a decrease in the initial shrinkage temperature, TZ3Y increasing the diffusion mechanisms responsible for densification.

Already in figure 2.b is observed na atypical behavior in the shrinkage curves as a function of temperature for β-alumina samples (100%β). They demand higher temperatures for the same densification levels. We found that the modified composition 100βCM sample (10,5% Na_2CO_3.1%$Mg(OH)_2$.88,5%Al_2O_3) causes a decrease in the initial shrinkage temperature compared to the nominal composition sample 100βCN(8,5%Na_2CO_3.1%$Mg(OH)_2$.90,5%Al_2O_3).

(a)



(b)

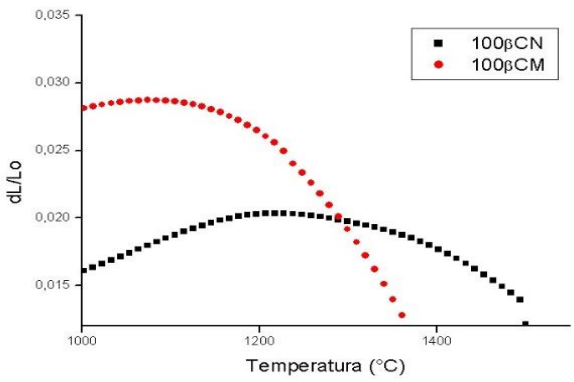


Figure 2: Linear shrinkage (a) Na-β-alumina/TZ3Y composite for samples 95β5Z, 85β15Z, 75β25Z and (b) Na-β-alumina: 100βCN

and 100βCM as function of temperature heated to 1500°C for 2h with heating rate 5°C/min.

The retraction onset temperature for 100βCM, 100βCN, 95β5Z, 85β15Z and 75β25Z samples heated at 1500°C for 2h with heating rate 5°C/min are shown in Table 1.

Table 1 – Retraction onset temperature for 100βCM, 100βCN, 95β5Z, 85β15Z and 75β25Z samples heated at 1500°C for 2h with heating rate 5°C/min.

Samples	Temperature onset retraction (°C)	Total retraction
100βCM	1325,83	0,01938
100βCN	1188,93	0,02680
95β05Z	1302,02	0,01440
85β15Z	1250,73	0,01220
75β25Z	1203,23	0,01430

From the results of the impedance spectra, it was possible to determine the value of intragranular resistance with the aid of Zview software. Resistance values (R) were obtained to calculate the conductivity (σ) of the sample. The conductivity values of the Na-β-alumina sample are presented in Table 2.

Table 2 – Conductivity values of the Na-β-alumina sample at the following temperatures: 25, 50, 100, 125, 150 and 175°C.

Temperature (°C)	Conductivity ($S.cm^{-1}$)
25	$1,86x10^{-5}$
50	$7,78x10^{-4}$
100	$3,04x10^{-4}$
125	$4,70x10^{-4}$
150	$6,17x10^{-3}$
175	$6,40x10^{-3}$

As expected, the resistivity of the sample decreases with temperature, that is, its conductivity increases. According to Youngblood et al, the conductivity of beta-alumina would be 0,22-1 $S.cm^{-1}$ at 300°C[2]. Wang found the electrical conductivity of $1,085x10^{-2}$ $S.cm^{-1}$ at 300°C[3] lower than the value found in this paper since the maximum test temperature was 175°C.

Conclusions

It was possible to identify and verify the formation of the desired phases β/β´´-alumina presente in the solid electrolyte Na-β-alumina

The presence of ytria stabilized zircônia (TZ3Y) caused a decrease in the initial shrinkage temperature, TZ3Y increased the diffusion mechanisms responsible for densification.

Its verified that the electrical conductivity of the Na-β-alumina electrolyte decreases to 100°C, after this temperature the resistivity of the sample decreases, that is, its conductivity increases.

Acknowledgments

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