

SYNTHESIS OF β -ALUMINA SOLID ELECTROLYTE FOR SODIUM-SULPHUR BATTERIES

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ABSTRACT

β -alumina is a sodium ion conducting solid electrolyte with an ideal formula $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$. It has another phase namely β'' alumina ($\text{Na}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$) wherein Na_2O content is more and has a greater conductivity than beta Al_2O_3 . Distinctions between β and β'' Al_2O_3 are given in this paper. Various methods of synthesizing the above powders and sintering to get one end closed tubes are discussed here for their use in sodium-sulphur batteries.

Key words: β -alumina for sodium-sulphur batteries

INTRODUCTION

β -alumina reported in 1967 [1] is a ceramic solid electrolyte in which the mobile sodium ions move as in a liquid [2] and has the highest sodium ion conductivity among all the identified solids [3]. These compounds are receiving special attention at present for use as a separator cum solid electrolyte in high energy and high power density batteries.

The various methods of synthesis of β and β'' alumina powders, their distinction and characterisation, the fabrication of wares using β/β'' alumina powders, the sintering and the determination of their conductivity are discussed in this paper. The different applications of β alumina solid electrolyte and the modes of its failure in service are, besides, described.

β and β'' alumina

The general formula of β alumina class of compounds is $\text{M}_2^I\text{O}_x\text{M}_7^{\text{III}}\text{O}_3$ where x varies from 5 to 11 [4]. M^I is a monovalent cation and M^{III} is a trivalent cation. In all these compounds spinel-like blocks are separated by planes where monovalent cations and oxide ions are loosely packed. In sodium β alumina, NaO layers and spinel blocks of $\text{Al}_{11}\text{O}_{16}$ are stacked alternately. The monovalent cations are mobile in the direction of the plane itself while mobility in the normal direction is negligible. The ideal formula for sodium β alumina ($\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$) is never reached in practice and depending upon the Na:Al ratio, the compound is said to exist in two phases viz. β and β'' where β'' ($\text{Na}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$) is richer in sodium. The distinction between β and β'' alumina is presented in Table I.

Table I: Difference between beta and beta'' alumina

β alumina	β'' alumina
1. Na-Al ratio 1:7 or 8 (Na_2O content 3.24%)	Na-Al ratio 1:5 (Na_2O content 10.8%)
2. Conduction is less, 10-15 $\Omega\text{-cm}$ at 350°C	Conduction is more, 6-7 $\Omega\text{-cm}$ at 350°C
3. Two spinel blocks in unit cell	Three spinel blocks in unit cell
4. In the Na-O plane there is a fixed site for Na. So energy is more for migration	In the NaO plane, no fixed site for Na. All are equal. So more freedom and conduction
5. Stable above 1500°C	Metastable above 1500°C. So dopants like MgO , Li_2O are added to stabilise this phase
6. Oxygen sequence near the axial plane has an eclipsed configuration	Staggered configuration
7. Hexagonal structure	Rhombohedral structure

Synthesis of β and β'' alumina powder

The different methods of synthesis are given below:

1. Vibromilling alumina and sodium aluminate [5]: Grinding and homogenisation are achieved by vibromilling α - Al_2O_3 and NaAlO_2 for a period of 48 hours with α - Al_2O_3 cylinders as grinding media. Dry milling minimises contamination due to self grinding of the media and produces powders having excellent compaction properties.

2. α -alumina and sodium added as sodium carbonate or sodium hydroxide with other additives like magnesium oxide or lithium oxide are wet-ball-milled for 2 to 6 hrs to form a slurry. This is spray-dried to obtain free flowing powder.

3. Sodium carbonate and alumina powders are mixed to provide a mixture equivalent to 60 wt% NaAlO_2 and 40 wt% $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ and heated to 1593°C, melted and cooled to room temperature. The particles of sodium β alumina embedded in sodium aluminate are produced. The sodium aluminate is dissolved in water, the rest ground or milled and sintered.

4. When nitrates, oxalates and alkoxides and hydrated salts of the respective elements are melted at 100°C and decomposed at 1200°C, the powders are obtained in intimately mixed condition. No sintering takes place during calcination. The product is of micron size and could be easily ground to still finer sizes.

5. In organic gel process water solutions of sodium, lithium and aluminium citrates with excess citric acid are gelled with ethylene glycol by evaporation followed by decomposition which results in β alumina powder.

In a method known as 'zeta process', zeta lithium aluminate [6] ($\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$ - pre-reacted Li_2O and α - Al_2O_3) is directly added to the calcined mixture of α -alumina and sodium carbonate. A uniform distribution of Li_2O (0.7-0.8%) is achieved in the powder compact. The product conforms to β'' alumina composition.

At the Central Electrochemical Research Institute, Karaikudi (CECRI) the methods adopted include the decomposition of the sulphate mixtures and the Zeta process. Although the former method gave a fine powder of 1 mm size, it was given up because it was not found to be a viable process for scaling up. The Zeta process was hence retained.

Characterisation

The powders were analysed by chemical analysis for their composition and by x-ray for identification. The characteristics of the powders synthesized at the CECRI are presented in the Table II.

Table II: Values of 'd'_{obs} obtained from x-ray powder diffraction data of the sample containing Na₂O 8%, MgO 2% and Al₂O₃ 90%*

d _{obs} Å	d _{obs} Å
11.31 p	2.41 p
5.85 p	2.33 p
4.82	2.24
4.31	2.15
4.80	1.97
2.80 p	1.81
2.78	1.60
2.68 p	1.58
2.60 p	1.54
2.51 p	1.48
	1.40

* Section 19 card 1174 x-ray powder data identified as sodium β alumina.

Structure

The β alumina structure is hexagonal [7]. Its unit cell is composed of two spinel blocks separated by a mirror plane. They are stacked alternately. In spinel like plane, four oxygen layers are packed closely and some Al³⁺ ions are tetrahedrally surrounded and the others octahedrally surrounded by O²⁻ ions. The structure of the block is similar to that of spinel MgAl₂O₄, if Mg²⁺ ions are replaced by Al³⁺ ions. In the NaO layers, oxygen ions are packed loosely leaving many available sites for sodium ions and only a part of them are actually occupied by sodium ions. The lattice constants are a = 5.59 Å and c = 22.53 Å. This is popularly known as two-block β alumina. The ideal composition is Na₂O.11Al₂O₃.

The β alumina structure is rhombohedral and the lattice constants are a = 5.59 Å and c = 33.95 Å. Three spinel blocks are stacked and this structure is identified as three-block β alumina. Its ideal composition is Na₂O.5.33Al₂O₃ [8].

In both β and β alumina the conduction planes are 11.3 Å apart.

Dopants

Dopants (i) stabilise β phase (ii) divalent cations substitute Al³⁺ ions in the spinel block resulting in the introduction of excess Na⁺ ions in the NaO layer to maintain charge neutrality and thus increase the conductivity.

Li⁺, Mg²⁺, Ni²⁺, Co²⁺, Cu²⁺, Zn²⁺, Mn²⁺ and Cd²⁺ stabilise the β alumina structure and increase the conductivity [9]. In contrast Pb²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ are not able to stabilise β phase.

Over-doping weakens the ceramic [10] and it is rapidly attacked by moisture [11]. From the studies [12] made the following conclusion is noted:

Lithia-doped β alumina is not suitable for sodium-sulphur battery to be operated over a long period. The dissolved lithium ion substitutes sodium ion in β and β ceramic causing the expansion of crystal structure thus resulting in strain and fracture.

MgO dopant is found to be stable at the sintering temperature and is resistant to corrosion.

Methods of forming β alumina tubes

(i) Electrophoretic deposition

This is considered a simple and rapid method, in which pre-reacted β alumina powder is suspended in a suitable liquid (generally organic) and made to get deposited on a steel/graphite mandrel by applying a D.C. voltage between the mandrel and the counter electrode [13]. From the steel mandrel the tube is removed whereas the graphite mandrel is burnt to get the tube.

The two suspensions usually employed in the above process are:

(a) 40 g β alumina powder in 500 ml of dichloromethane [14] containing 3 to 6 g of trichloroacetic acid is ball-milled for 8 hours using porcelain balls as grinding media or (b) 200 g β alumina powder in 200 ml of normal amyl alcohol [15] containing 0.25 g aluminium stearate is ball-milled for 16 hours and diluted to 200 ml as additional vehicle.

(ii) The plasma spraying [11] of pre-reacted β alumina has been studied. At the temperature of the plasma gun there is a significant loss of NaO even during the short duration of heating of the powder. This route is not followed at present.

(iii) Cold isostatic pressing or wet bag tooling

In this technique [16], the powders contained in a shaped rubber bag with the steel mandrel are compacted by applying hydraulic pressure (150-400 MN/m²) to the outside of the bag. Here high density and good dimensional tolerance are achieved. Closed end tubes with thin walls and lengths of over 500 mm can be fabricated and for wall thickness less than 1 mm the green shapes can be machined. The principal requirement for isostatic pressing is a free-flowing powder that will fill the mould cavity with a reproducible quantity of powder.

By this technique, tubes of 15 mm O.D, 12 mm I.D. and 100 mm length have been fabricated at CECRI Karaikudi.

(iv) Hot isostatic pressing

A pressure vessel containing internal heaters is used [17]. Inert gases (usually argon or helium) is pumped through compressors into the pressure vessel. The powder is introduced through SCR devices and controlled by the thermocouple outputs against the set values. The pressure vessel may be of monolithic, segmented or wire-wound construction. It is reported that facilities are available for hot isostatically pressing the tubes at 2 k bar (2000 kg. cm⁻²) at 1450°C.

(v) Doctor blade method

The ceramic tapes formed by this method [10] are used to form cylindrical one-end closed tubes by wrapping the tapes around the mandrel. The powder is mixed with a thermoplastic organic resin, a compatible plasticizer, a solvent and a wetting agent in a grinding jar. Approximately 0.1 mm thick sheets are formed by doctor blading the slip onto a polyethylene coated paper fixed to a glass sheet. They are then stripped from the paper.

Sintering the tubes

Two types of sintering are generally followed: (i) zone sintering and (ii) programmed sintering [11].

In zone sintering, the tubes are passed, rapidly through the hot zone of 1700°C (40-50 mm/minute). Firing at this maximum temperature is done for a period of 5 to 10 mts. Here, densification is rapid. Exaggerated grain growth is repressed. The short buffered firing cycle prevents the loss of Na₂O through volatilisation.

In programmed sintering the tubes are kept in sealed containers of platinum, MgO or Al₂O₃ to prevent Na₂O loss and stacked in the furnace. The temperature is slowly raised and then cooled according to prearranged temperature-time cycle which is of the order of 16-24 hours. The maximum temperature is usually in the range 1600-1650°C.

Seeding of oxides

Recent work has indicated that the addition of 10% β alumina as nucleating agent favours the conversion of precursor oxides to β alumina through a catalytic action [7]. Besides densification, a reduction in electrical resistivity at 300°C viz. 5.3 ohm-cm in comparison with 12 ohm-cm for the unseeded material is achieved. But the crystal size is increased from 0.2 μ m to 20-60 μ m along with reduction in tensile strength from 250 MN/m² to 170 MN/m². Further detailed study is required to obtain improvement in conductivity without further grain growth.

Fine-grained microstructure is desirable for high strength and homogeneous current flow. Exaggerated growth of some grains leads to duplex morphology. Only a very precise control of the sintering cycle

enables one to achieve high conversion to the desired β phase without overdoping and oversintering.

Porosity

The tubes should be tested for porosity with impermeability to helium gas and the application of such tubes will result in better operation of the sodium-sulphur battery.

Electrical conductivity

Both a.c. and d.c. methods are used [7]. In the d.c. method sodium metal is filled both inside and outside of the tubes. In the a.c. method, using Na and $\text{NaNO}_3/\text{NaNO}_2$ mixture, resistivity measurements are performed with platinum or gold as electrodes at high frequency. Care is necessary to obtain good contact between β alumina tubes and electrodes. Argon atmosphere should be maintained for sodium electrodes in both the methods. Though β'' alumina has higher ionic conductivity than β alumina, it is inferior in mechanical strength, thermal shock resistances and electrochemical degradation resistance in molten sodium due to large grain size. This was responsible for the use of β alumina in Government projects in spite of its lower ionic conductivity [12].

Modes of failure

i) Electrical breakdown: This results because of localised high current density [11] during short circuit by sodium dendrite [18] penetration from negative to positive electrode.

ii) Mechanical breakdown: This results due to intrinsic defect in the tube or externally applied mechanical shock.

iii) Thermal breakdown: This results due to mismatch in the expansion between β alumina tube and the seal. Cracking occurs near the seal at a temperature below 150°C . Recent studies indicate that most of the failures are attributed to the solid electrolyte tube [19].

Mechanism of conduction

In β alumina, sodium is distributed over three positions [20]. Beever's-Ross sites, Midoxygen sites and anti-Beever's-Ross sites. The BR sites have the largest fraction of the sodium ions, 60% and are considered to be regular sites. The anti-BR sites are hardly occupied but due to space requirements can only be occupied when the sodium at a regular BR site is also displaced towards another MO site. The two neighbouring occupied MO sites are to be considered as an interstitialcy at a BR site.

β alumina was proposed as a sodium ion conductor and nonstoichiometric compound possessing high vacancy concentration in 1960.

Cation diffusion in β alumina occurs by an interstitialcy mechanism [21] in which a cation on an interstitial site jumps to a regular site ejecting the ion there to the second interstitial site.

The conduction in β'' alumina phase which contains significantly higher alkali concentration is believed to occur by a vacancy mechanism.

It is not possible to say unequivocally [22] which mechanism viz. vacancy mechanism or interstitialcy mechanism prevails in β alumina. Only approximate equations have been given for both vacancy and interstitialcy mechanisms and these are temperature-independent whereas the values of Haven ratio obtained are temperature dependent

$$\text{Haven ratio, } H_R = D_i/D \text{ where}$$

D denotes diffusion coefficient obtained from ionic conductivity, and D_t denotes diffusion coefficient obtained from tracer diffusion.

Application of β alumina

β alumina finds application in the following:

- i. Separator cum solid electrolyte in sodium-sulphur and sodium-chlorine battery
- ii. Membrane in thermoelectric converters
- iii. Production of rayon-grade caustic soda
- iv. Sodium-ion probe in molten aluminium and its alloys and
- v. On-line monitoring of sodium vapour pressure in argon atmosphere in the Fast Breeder Reactors.

Conclusion

Considering the various aspects of synthesis and fabrication of β alumina solid electrolytes and their electrical, thermal, mechanical, thermomechanical and chemical behaviour in operation, it is felt that MgO doped β alumina tubes made by hot isostatic pressing could be highly suitable for application in sodium-sulphur batteries.

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