# SURFACE EFFECTS IN BETA-ALUMINA SYNTHESIS AND SINTERING FOR ELECTRONIC APPLICATIONS

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#### RESUME

Solar and wind are clean, powerful and alternative sources of energy, despite intermittent. To provide a constant energy supply, one solution is an effective largescale storage of the surplus energy generated at peaks of production and its release when needed. Electrochemical systems or batteries are capable of reversibly storing and releasing electrical energy with high efficiency. The most used batteries are based on a solid electrolyte membrane of beta-alumina. It is well-known that properties of ceramics like beta-alumina are highly dependent on their microstructure and powder surface characteristics. When dopants are added, they can diffuse into the crystal bulk forming a solid solution, migrate to the surface or nucleate as a second phase. As beta-alumina needs dopants to phase stabilization, it is submitted to surface segregation, which modifies its surface energy, particle size and consequently phase transformation temperature. The aim of this study is to evaluate the effects of dopants such as Mg on the thermodynamic properties of beta- alumina synthesized by Pechini's method and its influence in the electronic properties. So far, it was possible to observe that the surface energy, modified by adding dopants, is determining the system's phases stabilities. Also the phase stability of the hexagonal and rhombohedric beta-aluminas is being affected.

Key words: beta-alumina, dopants, surface effects.

### INTRODUCTION

The concern over the use of fossil fuels and environmental preservation has influenced the search for new energy sources that are at the same time powerful, renewable, clean and environmentally friendly.

In this context, energy sources such as the wind and the sun emerge as powerful alternatives despite their intermittence. During the interruption, the energy provision must continue so one of these cannot be the only power source.

An alternative to provide constant energy supply is to storage the surplus energy produced at the peaks of production using batteries. These batteries are chemical systems that are able to store energy and release when needed.

The most used batteries nowadays are based in a ceramic electrolyte. Although ceramics are not known as good conductors, the ionic diffusion normally occurs in all solids, including ceramics. However, diffusion mechanism normally takes place through vacances and has to overcome high energy barriers, which results in low ionic mobility. Some solids, on the other hand, are known as "ionic superconductors" and presents high ionic conductivity and major field of applications [1].

Ceramic electrolyte consists in a thin membrane that allows charge transportation between the electrodes. Among all the possible conductor materials,  $\beta$ "-alumina is the most common. The charge transport is made via Na<sup>+</sup> cations diffusion. Due to the type of electrolyte used, these electrochemical devices are often referred as Na-beta batteries (NBBs) [2].



**Figure 1.** Single-cell and tubular design of an NBB battery and electrode [2].

 $\beta$ "-alumina is a mix of aluminum and sodium oxides, resulting in a nonstoichiometric alumina doped with sodium presenting particular atomic structure.



Figure 2. Beta-alumina crystal structure [3].

Close-packed layers containing aluminum (tetrahedral and octahedral interstices) and oxygen atoms in a spinel-like structure are alternated with loosely packed layers where the mobile sodium cations are free to movement under an electric field.

 $\beta$ "-alumina (rhombohedral) is the preferred polymorph since its unit cell is 50% large than  $\beta$ -alumina (hexagonal), and therefore, it presents a higher conductivity.

 $\beta$ "-alumina is unstable above 1450°C, being frequently doped with magnesium (Mg) and/or lithium (Li) to promote stability at high temperatures, otherwise, it is irreversibly transformed into  $\beta$ -alumina.

For the past decades has been a lot of progress in the studies about NBBs, but yet the material's performance and production costs are still holding back the advances [2].

Properties of ceramics, such as beta-alumina, are highly dependent on their microstructure and powder surface characteristics, as chemical groups and surrounding interactions [4]. According to the desired final properties to a specific application, it is possible to adjust the production process to obtain the better final product.

It is known that when dopants are added, they can follow different paths: (1) form a solid solution in the crystal bulk (2) nucleate as a second phase or (3) spontaneously migrate to the particle interface and segregate as an attempt to lower the surface energy. However, ions only segregates if the surface energy decrease is greater than the bulk energy decrease in the case of a solid solution formation [5].

From this point of view, the surface physical-chemical study can help to explain the synthesized material final properties. Sinterization is also subjected to this approach. Normally, synthesis and sinterization processes are treated exclusively as kinetics phenomena and little or none of thermodynamics are given attention, especially when there are non-extensive solid solutions and the occurrence of surface segregation causing the, so called, surface effects. These effects must alter the material surface energy, and therefore, the phase stability [5].

Since dopants are needed to  $\beta$ "-alumina phase stabilization, the role of surface segregation, which modifies the surface energy of nanoparticles, has been studied in our work. The dopants effects on the polymorph stability and powder characteristics of beta-alumina synthesized by Pechini's method have been verified.

### MATERIALS AND METHODS

 $\beta$ "-alumina powders were prepared via resin synthesis, according to the Pechini's method [6]. Blended in the desired concentration of each cation, the polymeric precursor was calcined first at 450°C, then at 650°C for 15 hours to particle size stabilization.



Figure 3. Polymeric precursor heating program.

The samples were finally heated to  $1250^{\circ}$ C to obtain the  $\beta$ "-alumina phase and characterized by: Thermal analysis, X-ray Diffraction, Granulometry analysis, Specific surface area, Scanning electron microscopy and Fourier Transform Infrared Spectroscopy.

#### **RESULTS AND DISCUSSION**

The Mg doped  $\beta$ "-alumina (Na<sub>2</sub>MgAl<sub>10</sub>O<sub>17</sub>) was prepared with Al, Na and Mg resins, blended in the molar ratio of 10:2:1, respectively. The resulting powder was submitted to thermal analysis.



Figure 4. TG and DTA analysis.

Mass loss and signal until 450°C shows the evaporation and loss of absorbed and chemical bonded water. Above this temperature, the mass loss continues, so it must be an evidence of the decomposition of carbonates remaining from the resin pyrolysis. There are three remarkable exothermic peaks, at 700, 800 and 1170°C. X-ray diffraction was used to determine these transformations.

As shown in Figure 5,  $\beta$ "-alumina phase transformation only occurs above 1100°C. Intermediates appears about 700°C and, as the temperature increases, they are transformed into the final powders containing: Mg doped  $\beta$ "-alumina (rhombohedral),  $\beta$ -alumina (hexagonal) and Sodium aluminate.  $\beta$  and  $\beta$ "-alumina are

always produced together, which does not affect the final powder electrical properties.



Figure 5. X-ray diffraction patterns of powders calcined at various temperatures.

The Infrared spectrum, Figure 6, shows the particles surface evolution since it has been prepared. As the powder spends more time interacting with the atmosphere, it absorbs more water, –CO groups and carbonates. Water presence (liquid and dissociated -OH groups) are clearly notice from 3687 to 2850 cm<sup>-1</sup> and at 1640 cm<sup>-1</sup>; and CO groups and carbonates from 2500 to 2125 cm<sup>-1</sup> and 1430 cm<sup>-1</sup>. And finally, the oxygen-metal bonds vibrations are observed below 1000 cm<sup>-1</sup>.



Figure 6. Infrared Spectrum.

Resin originated oxides are nanometric since powder formation are based on nucleation while resin pyrolysis occurs. Final powder particle size distribution (Figure 7) is mostly around 100  $\mu$ m, but is possible to observe by Scanning Electron Microscopy (Figure 8) that a great number of agglomerates are present and hexagonal (highlighted) and needle-like particles are much smaller than 4  $\mu$ m. Particle size distribution is representing the agglomerates distribution, not particles.

57º Congresso Brasileiro de Cerâmica 5º Congresso Iberoamericano de Cerâmica 19 a 22 de maio de 2013, Natal, RN, Brasil







Figure 8. Scanning Electron Microscopy of calcined final powder.

Specific surface area is presented in Table 1. As temperature increases, agglomerates are formed and particles grow, decreasing specific surface area.

Table 1. Specific surface area.		
650°C	1250°C	
45.4 m²/g	4.0 m²/g	

## Additive's concentration

A decrease or enhancement in the additive's concentrations may affect the phase stability and powder characteristics. Two samples, one containing 0.5 and the other containing 1.5 moles of magnesium, were prepared to compare the phase formation and surface area.

The sample containing 0.5 molar ratio of Mg did not provide the desired powder, even though Mg- $\beta$ "-alumina was one of the obtained phases among other non-desirable oxides. In the other hand, 1.5 magnesium molar ratio has extrapolated Mg concentration's for  $\beta$ "-alumina, which has caused the formation of spinel (MgAl<sub>2</sub>O<sub>4</sub>) among Mg- $\beta$ "-alumina and  $\beta$ -alumina phases.

Table 2 presents specific surface area comparison.

Table 2. Mg-dopped samples specific surface area.		
Mg molar ratio	650°C	1250°C
0.5	61.1 m²/g	33.9 m²/g
1.0	45.4 m²/g	4.0 m²/g
1.5	54.7 m²/g	18.6 m²/g

Surface area analysis of these powders unfortunately cannot be conclusive in determining if the Mg ions are segregating in the surface because different phases

have different characteristic surface areas. An example is the high specific area presented by the 1.5 Mg-dopped sample, which would be an evidence of surface energy decrease, leading to less particle growth and high specific surface area. However, it is known that spinel presents high surface area and this enhancement could be only due to the spinel phase appearance.

Surface areas can only be compared to predict surface segregation if the same phases (and in the same proportion) are present.

A model to explain the dopants concentration relation to phase formation, surface area, and later, ceramic sintering are still in development to proceed with this work.

# CONCLUSION

Mg- $\beta$ "-alumina was successfully produced by Pechini's method. The nanometric particles surface presents groups that can change this area energy and influence in the phase stability depending on the additive's concentration.

A full model explaining dopants correlation to phase stability and particle size (specific surface area) is been developed in order to study and improve this material sinterization to present great performance as an ionic electrolyte.

## ACKNOWLEDGMENTS

CAPES; PMT-USP.

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