Thermochimica Acta, 85 (1985) 227—230
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THERMAL EVOLUTION OF Na(Li)POLYALUMINATE MICROSPHERES PRODUCED VIA A SOL-GEL METHOD

O. SBAIZERO
Applied and Industrial Chemistry Inst., University of Trieste (Italy)

ABSTRACT

Sodium aluminates are finding an ever expanding role as critical components in many high technology systems which are currently under development for energy application. Recently, sodium aluminates particles with equidimensional shape (i.e. spheres) have been produced by a sol-gel method. These powders are of interest for possible advantages in ceramic fabrication processes. The objective of the current investigation was to characterize the thermal evolution of these powders by thermal analysis, XRD, SEM and chemical analysis in order to determine their transformation trend and the final products' nature.

INTRODUCTION

Given the potential usefulness of beta-alumina ceramics as solid electrolytes a great deal of emphasis has been placed on the processing of these materials:

- the hexagonal form (β alumina = $Na_2O \cdot 11\ Al_2O_3$) (ref.1)
- the rhombohedral form (β" alumina = $Na_2O \cdot 5\ Al_2O_3$) (ref.1)

The β" form is normally stabilized by the addition of Li_2O or/and MgO (ref. 2) and its sodium ionic conductivity is higher than that of the β form (ref. 3).

Recently, solid electrolytes tubes made of Li stabilized β" alumina have been used (ref.4) but additional studies are required for the development of a manufacturing system suitable for mass production as well as for costs reduction. Numerous preparations have been attempted with variable results, among these, the sol-gel process has given promising results, e.g. control of particle size, shape and properties, good mixing for multi-component system, high reactivity of powders (ref. 5).

The aim of this investigation is to examine the thermal evolution of Na(Li)polyaluminate microspheres prepared by the sol - gel process* through the TG-DTA curves and chemical,XRD,SEM analyses, in order to determine their transformation trend and the final products' nature.

* Prepared at the E.N.E.A. laboratories in Rome

0040-6031/85/$03.30

METHODS

The gel was made according to Majani et al.(ref.6)and the dried powder, called Na(Li)polyaluminate, had the composition in weight%: Na_2O=8 Li_2O=0.8 Al_2O_3=91.2. Its spherical morphology is shown in Fig.1. The TG-DTA curves were obtained with a STA 409 V/3 Netzsch apparatus; atomic absorption and gas cromatography were used for chemical analysis. To study the crystallization behaviour of the powder synthetized in this study, samples were quenched from the TG-DTA apparatus at various temperatures between 680° and 1600°C. Following this calcination, the samples were examined using XRO and SEM to determine the phase content, size, shape and degree of crystallization.

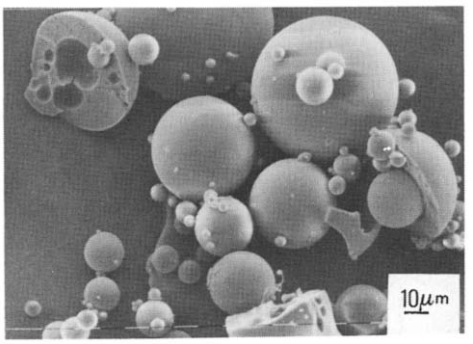

Fig. 1 Uncalcined spherical particles of Na(Li)polyaluminate

RESULTS AND DISCUSSION

The thermoanalytical curves of the crude powder and the X-ray diffraction patterns of samples calcined at various temperatures are presented in Fig. 2 and 3.

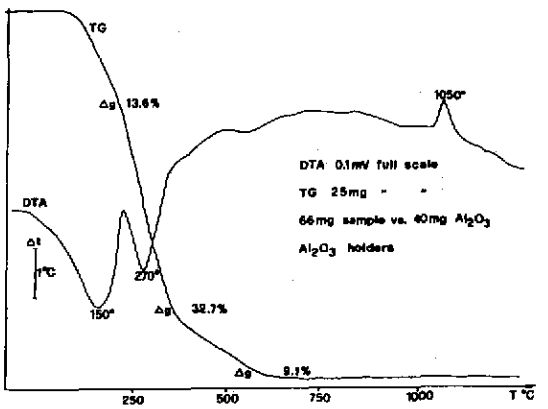

Fig. 2 TG-DTA curve for uncalcined powder

They revealed the following trend: the chemical analysys of the uncalcined powder indicates the presence of C=4.1(%weight), H=4.3% and N=5.02% due to the starting nitrate solution, a long-chain primary amine and the aliphatic alcohol used in the sol-gel process.

The DTA curve shows a first large, broad endothermic peak centered at∿ 150°C (see Fig.2). The chemical analysis indicates: C=1.82%, H=4.02%, N=4.87%. The TG curve shows a weight loss of 13.6% due primarily to aliphatic alcohol and water release. A second endothermic peak is observed, centered at ∿ 270°C (see Fig.2). From 200° to 360°C a sharp weight loss of 32.7% occurs. The chemical analysis: C=0.72 H=2.69%, N=2.08% indicates that hydroxide and nitrate release is confined to the next and last decomposition step. A gradual weight loss of 9.1% occurs in the 360°-680°C range. The total weight loss is about 55.4%. The chemical analysis at 680°C indicates only Na, Li and Al present. At 900°C the powder has a few broad, diffuse peaks corresponding to δAl_2O_3 (JCPDS 16-394) (see Fig.3). The exothermic peak centered at ∿ 1050°C in the DTA curve (see Fig.2) reflects the powders' crystallization. The XRD pattern shows that at 1200°C the material has peaks corresponding to β alumina and $NaAlO_2$ which appears as flakes on the spheres' surface (see Fig.4). The sample brought to 1350°C shows decreased peak intensities for β alumina and increased ones for β" alumina (see Fig.3). Peaks corresponding to $NaAlO_2$ are still detected but the SEM image indicates that this later compound has decreased on the spheres' surface. The XRD pattern at 1600°C shows peaks corresponding to β" alumina with a small β remanent. Highly crystallized material was obtained after a 6 h 1600°C treatment (see Fig.5). The spheres' morphology shows a coarse grained material whose geometrical feature corresponds to the crystalline structures of the hexagonal and rhombohedral beta aluminas.

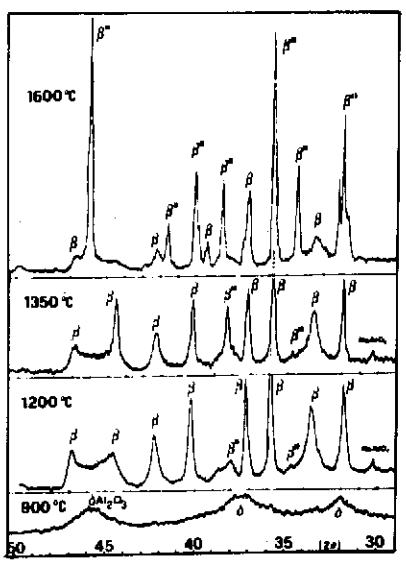

Fig.3 XRD for powder calcined at temperatures indicated

CONCLUSIONS

Spherical particles of Na(Li)polyaluminate produced by a sol-gel method were subjected to heat treatment at temperatures up to 1600°C. Uncalcined particles contained a significant amount of water and organic compounds derived from the

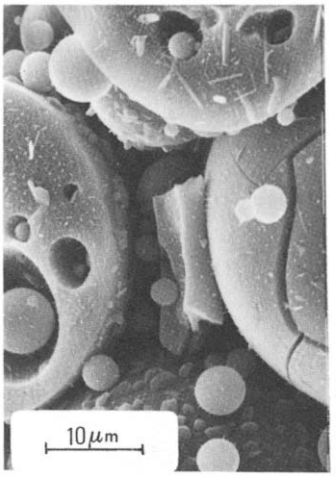

Fig.4 Powder calcined at 1200°C

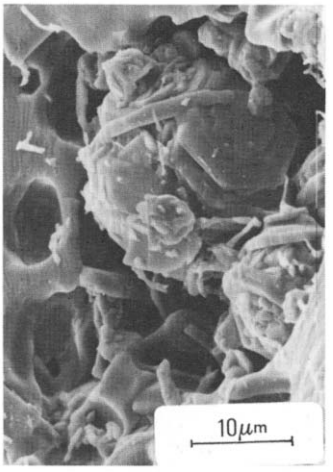

Fig.5 Powder calcined at 1600°C

sol-gel process. They were removed at temperatures below 600°C. The crystallization began at 1050°C and until 1200°C primarily β alumina formed with some $NaAlO_2$ on the spheres' surface. At 1600°C a large amount of β is transformed to the β" form with an extended grain growth phenomenon.

ACKNOWLEDGEMENT

The author wishes to thank Prof. S. Meriani for many helpful discussion.

REFERENCES

1 J. T. Kummer, Prog. Solid State Chem. 7 (1972) 141
2 Ford Motor Co., Annual Rept, NSF Contract NSF-C805, July 1974
3 T.J. Whalen, G.J. Tennenhouse, C. Meyer, J. Amer. Ceram. Soc. 57 (1974) 497
4 M.L. Miller, B.J. McEntire, R.S. Gordon, Amer. Ceram. Soc. Bull. 58(5)(1979) 522
5. J.L. Woodhead, K. Cole, J.T. Dale, E.L. Paige, in Science of Ceramics 12, Ceramurgia s.r.l., Faenza, 1984, pp. 179-185
6 C. Majani, M. Carewska, A. Deptula, RTI/CHI (83) 12