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β-ALUMINAS AND WATER
A comparison of mixed Li–Na and pure Li and Na β-aluminas

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CENTRO DI STUDIO PER LA TERMODINAMICA ED ELETTROCHIMICA
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TG, DSC and X-ray measurements were made to characterize the water absorption process by Li (50%) – Na (50%) β-alumina.

The equilibrium water content, dehydration enthalpies and lattice parameter values have been determined and compared with those previously obtained for pure Li and Na β-aluminas.

The mixed β-alumina is shown to be very similar to Li β-alumina as concerns the dehydration enthalpy and the temperature range in which the dehydration occurs, while it seems to be very similar to Na β-alumina with respect to the equilibrium water content and *c*-axis values.

The term β-alumina covers an entire family of solid electrolytes of general formula $(M_2O)_{1+x} \cdot 11\ Al_2O_3$, where x can vary within certain limits ($0.15 < x < 0.30$) and where M can be one of various monovalent and divalent cations. Each member of the family can be obtained by cationic exchange in molten salts. For hystorical [1] and technological [2] reasons the most important member of the family is Na β-alumina. It has been known for a relatively long time [3] that water can enter the lattice and affect the electrochemical properties of Na- and Li-containing β-aluminas. Nevertheless, a comprehensive view of the subject has not yet been obtained and many questions are still awaiting an answer, e.g. how much water can enter the lattice, how large its hydration enthalpy is, and the role played by the thermal treatment of the samples. When literature data do exist, they are contradictory as concerns the maximum water content [3, 4]. This uncertainty in such a basic parameter as the equilibrium water content may perhaps explain the slow development of the entire subject.

In our opinion too little attention has been paid so far to the kinetic aspects of water uptake by β-aluminas: our results demonstrate that this process is a very slow one and samples of very small grain sizes must be used to attain the equilibrium water concentration with reasonable hydration rates at room temperature [5]. With this in mind, meaningful results can be obtained and the interaction of β-aluminas with water is no longer an insoluble problem, but only a difficult problem.

Thermogravimetry, differential scanning calorimetry and X-ray diffractometry were used to characterize the interaction between Li–Na β-alumina and atmospheric moisture. The results are reported here and compared with those obtained for pure Li β-alumina and pure Na β-alumina, some of which already been published [5, 6] and some of which will soon be published [7].

Experimental

Both Li and Li–Na β-aluminas were prepared by cation exchange in molten nitrate baths, using as starting material a melt-grown Na β-alumina single crystal supplied by Union Carbide. The sodium excess of the starting crystal and the extent of cation substitution were controlled by measuring the weight changes during several complete substitutions of Na^+, $Li–Na^+$ or Li^+ by Ag^+ and by neutron activation analysis. The following formula for our β-aluminas was obtained by both methods: $(M_2O)_{1.22} \cdot 11\ Al_2O_3$ where M can be pure Na, pure Li, or Li (50% by mole) + Na (50% by mole). All measurements were performed on finely-divided crystals obtained by grinding the original or exchanged single crystal and then by screening the material to the desired sieve fraction (less than 44 μm).

The TG and DSC measurements were made with the microprocessor-based Du Pont 1090 Thermal Analysis System equipped with the 951 Thermogravimetric Analyzer and with the 910 Differential Scanning Calorimeter.

Heating and cooling rates were selected to ensure the same water content, at the same temperature, both in the TG sample and in the X-ray sample. Taking as reference the isothermal cycle of the X-ray measurements, it was shown that no variation in water content occurs in dynamic thermal cycles with heating-cooling rates up to 1 degree/min.

As concerns the X-ray measurements, a home-made polythermal attachment [8] was used in conjunction with a Phillips PW 1011 diffractometer, utilizing Cu K_α radiation. In this way it was possible to make measurements in air or under vacuum (10^{-5} mm Hg pressure) in the entire temperature range of our interest.

As for Na and Li β-aluminas the crystallographic data of Peters et al. [9] were used for indexing, and corrections were applied for specimen displacement and thin-sample aberration [10] before lattice parameter values were obtained by standard least square analysis of the data

Results and discussion

It was shown for pure Na β-alumina [5] that the water uptake process consists of two steps: a fast one, for which a model was proposed, and a slow one governed by a diffusion law that makes the equilibrium water content practically unattainable in millimeter-sized crystals. Similar results have been obtained for pure Li β-alumina for which, although a more complicated situation arises, two different water absorption rates undoubtedly exist [7]. It is not surprising then that for Li—Na β-alumina too the overall process of water uptake is a slow one and several weeks of exposure to atmospheric moisture are required at room temperature to reach the equilibrium water content for our finely-divided crystals.

In Fig. 1 are reported the first two thermal cycles for a Li—Na β-alumina sample originally equilibrated at room temperature. The second thermal cycle was performed immediately after the first one. It can be seen that, although hysteresis effects are present, a fixed water amount (2.5% by weight) is gained or lost during the second thermal cycle, and that only the first heating involves a greater water loss (3.6%).

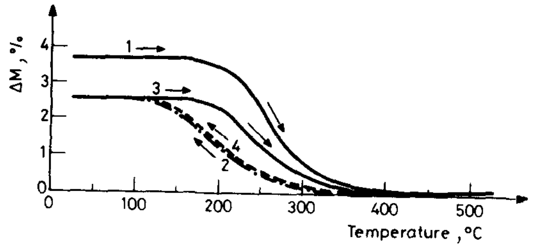


Fig. 1 Thermal cycles for Li—Na β-alumina. Solid lines represent first and second heatings. Dashed lines represent first and second coolings. The second cycle was performed immediately after the first one

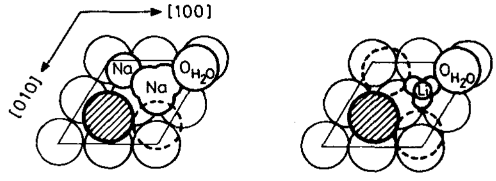
If after one or more thermal cycles, the sample is allowed to attain the equilibrium water content, i.e. it is left in air, at room temperature, for some weeks, a weight loss of 3.6% can again be observed on heating. This clearly indicates the presence in Li—Na β-alumina too of two different steps in the process of water absorption.

Table 1

	Maximum water content, %	Water "reversibly" exchanged, %
Li	6.2	3.5
Li—Na	3.6	2.5
Na	3.2	1.5

Table 1 summarizes our data with respect to the maximum water content (first heating of room temperature equilibrated samples) and water "reversibly" exchanged (second and further cycles). It may be noted that nearly twice the water contained in Na β-alumina can enter the lattice of Li β-alumina. To explain this difference, Fig. 2

reports scale drawings of the mirror planes of pure Li and pure Na β-aluminas. Details on the structure of β-aluminas can be found elsewhere [6]; here we recall only that there are two mirror planes per elementary cell and that they contain the columnar oxygen (the shaded circles in Fig. 2), the metal ions and the water oxygen. The positions of the species and the percentage occupations of the sites have been determined by refined structural analysis. From Fig. 2 it is easy to see that the mirror plane of the Li β-alumina is able to contain twice as much water as the Na β-alumina mirror plane. This analysis can no longer be applied to Li–Na β-alumina because of the lack of the site distribution and occupancy factor data for Li^+–Na^+ ions in this compound.



Naβ Liβ

Fig. 2 Mirror plane of Na and Li β-alumina hexagonal cells. The Na^+ ions are distributed near BR (close to water oxygen) and in mO sites. The Li^+ ions are centred around the BR position. The shaded circles represent the columnar oxygen. The dashed circles indicate sites available to water oxygen

In fact (Table 1), Li–Na β-alumina shows a behaviour exactly halfway between those of pure Li and Na β-aluminas as concerns the water "reversibly" exchanged, but it seems to be very similar to Na β-alumina in maximum water content. Why the presence of Na^+ ion affects the equilibrium water content in a more than proportional way is not yet completely clear. However, indications have been found by Wang et al. [11], that, as a consequence of the formation of Li^+–Na^+ pairs, in Li–Na β-alumina the alkali metal ions occupy positions somewhat different from those in pure Li and Na β-aluminas, with the Li^+ ion displaced toward the columnar oxygen and a greater percentage of the Na^+ ion near to the mid-oxygen (mO) sites. As the water oxygen too occupies mO sites, this ion displacement could possible explain the experimental value of the equilibrium water content in Li–Na β-alumina.

An analogous situation of a non-linear relationship between the cationic composition and the properties of Li–Na β-alumina has been observed with respect to the hydration-dehydration enthalpies. Our data relate to the dehydration enthalpies as determined by DSC on samples equilibrated at room temperature and so containing the equilibrium water concentration; values of 14.5, 13.5 and 10.0 (kcal/mole H_2O) were obtained for Li, Li–Na and Na β-aluminas, respectively, indicating a major role of the Li^+ ion in determining the energetics of the overall water uptake. The X-ray measurements are discussed with the aid of Figs 3 and 4. As for Li and Na β-aluminas,

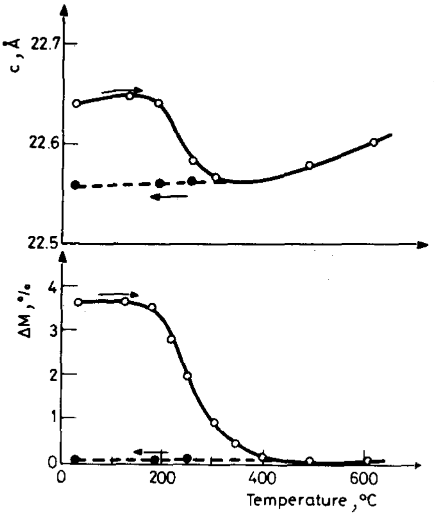


Fig. 3 Comparison of water content and *c*-axis value. Empty circles: first heating in air of originally equilibrated samples. Filled circles: cooling under vacuum

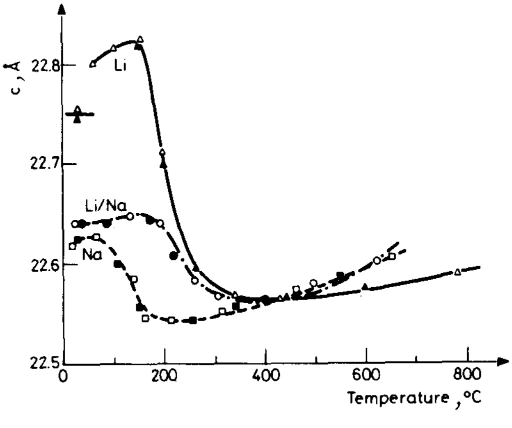


Fig. 4 *c*-axis values as a function of temperature. Triangles, circles and squares refer to Li, Li—Na and Na β-alumina, respectively. Empty symbols: first heating of originally equilibrated samples. Filled symbols: cooling and further heating

a relationship was found in Li–Na β-alumina between the water content and the *c*-axis value. The results are shown in Fig. 3. Here the water content of the X-ray sample can be deduced, at each temperature, from the TG curve. It appears from Fig. 3 that when no water is present (cooling under vacuum), the *c*-axis values are low but, differently from what one could expect, no simple relationship exists (see Fig. 4) between the water content and the *c*-axis value. This is the case for pure Li and Na β-aluminas too. Figure 4 compares the *c*-axis values as a function of temperature for the three β-aluminas. It can be seen that the *c*-axis values determined during the first heating of the samples lie on the same curve as those measured during cooling of further heating. This clearly suggests that only part of the total water affects the *c*-parameter values. Figure 4 also shows that Li–Na β-alumina is very similar to Na β-alumina as concerns the maximum Δc value, while it is very similar to Li β-alumina with respect to the temperature range in which the *c*-axis variation occurs. This last observation confirms the DSC results indicating the Li^+ ion as mostly responsible for the energetics of the water uptake by Li–Na β-alumina. On the other hand, the similarities between Na and Li–Na β-aluminas in maximum Δc value and maximum water content indicate that Na^+ ions play a major role in determining the maximum water amount that can enter the lattice of Li–Na β-alumina.

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Zusammenfassung — Zur Charackterisierung des Wasseradsorptionsprozesses an Li(50%)–Na(50%)-β-Aluminiumoxid wurden TG-, DSC- und Röntgendiffraktionsmessungen ausgeführt. Der Gleichgewichtswassergehalt, die Dehydratisierungsenthalpien und die Gitterparameter wurden bestimmt und mit denen früher für reines Li- und Na-β-Aluminiumoxid erhaltenen Werten verglichen. Was die Dehydratisierungsenthalpie und den Temperaturbereich der Dehydratisierung betrifft, so verhält sich das gemischte β-Aluminiumoxid sehr ähnlich dem Li-β-Aluminiumoxid, während es hinsichtlich des Gleichgewichtswassergehaltes und der Gitterkonstante *c* dem Na-β-Aluminiumoxid sehr nahe steht.

Резюме — С целью определения процесса поглощения воды смешанным Li(50%) — Na(50%) β-алюмином, проведены его ТГ, ДСК и рентгенографические исследования. Определено равновесное содержание воды, значение энтальпии дегидратации и параметр решетки. Полученные результаты сопоставлены с ранее полученными для чистых Li и Na β-алюминов. Относительно энтальпии дегидратации и температурной области, в которой происходит дегидратация, смешанный β-алюмина подобен чистому Li β-алюмину. Значения равновесного содержания воды и величина постоянной решетки вдоль *c*-кристаллографической оси для смешанного алюмина подобны чистому Na β-алюмину.

AICAT material is finished.