

# THERMAL STABILITY OF BETA"-ALUMINA SOLID ELECTROLYTE UNDER AMTEC OPERATING CONDITIONS

Roger M. Williams, Margie L. Homer, James Kulleck, Liana Lara, Adam K. Kisor, Roger H. Cortez, Virgil B. Shields, and Margaret A. Ryan  
*Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109*

**Abstract.** A critical component of alkali metal thermal-to electric converter (AMTEC) devices for long duration space missions is the sodium beta"-alumina solid electrolyte ceramic (BASE), for which there exists no substitute. The major phase in this ceramic, sodium beta"- alumina shows no evidence of thermal decomposition in AMTEC environments including clean liquid sodium and low pressure sodium gas, at temperatures below 1173K, or in vacuum below 1273K. This paper presents additional results of ionic conductivity and exchange current studies in sodium exposure test cells (SETCs) to characterize the changes occurring in BASE below 1273K in low pressure sodium vapor. Also presented are additional annealing studies to characterize the kinetics of processes occurring in in the BASE ceramic in the AMTEC operating regime.

## INTRODUCTION

The Jet Propulsion Laboratory has been investigating the degradation of critical AMTEC operating components under accelerated conditions for several years. The thermochemical data available and the phase relations of beta"-alumina, beta-alumina, and alpha alumina suggest that slow sodium oxide loss from beta"-alumina might be possible at AMTEC operating conditions, above 973K, especially at the higher temperatures up to 1223K. (Rog, 1992; Duncan, 1988; Williams, 1997) Experimental studies have shown that BASE is converted to alpha alumina at the surface when heated to 1273K or higher in vacuum for 100-500 hours. (Williams, 1998; Williams 1999) However, experiments have not revealed any decomposition of the sodium beta" alumina phase in BASE at temperatures of 1173K and below in vacuum or in low pressure sodium gas or in liquid sodium, except under conditions where reactive metals such as Ca, Cr, or Mn come into contact with the BASE. (Ryan, 1994; Williams 1995; Williams, 1998; Williams, 1999) Several earlier studies have demonstrated that interconversion of the beta, and beta"-alumina, and alpha alumina and sodium aluminate are kinetically slow at temperatures below 1600K, and apparently negligible below 1200K for exposure times of hours. (Kummer, 1972; Youngblood, 1977; Hodge, 1983; Hodge,1984; Mosely 1985) We cannot rule out minor loss of sodium oxide from the beta"alumina phase, if it occurs without a phase change. Nor can we rule out extremely slow decomposition of sodium beta" alumina which has been too slow to detect in our tests. However, in the event of very slow, highly activated loss of soda from the beta" alumina phase we would expect surface formation of degradation products, resulting in a decrease in the exchange current of stable electrodes on BASE. This would also be the most critical failure mode for BASE other than complete phase decomposition. If a few percent of the beta"alumina phase in the solid electrolyte ceramic were converted to a non-conducting form, distributed homogeneously throughout the ceramic, the solid electrolyte would still function, with slightly higher resistance. However, formation of an insulating layer on the order of 1.0nm at the surface would reduce the electrode/electrolyte interface's exchange current substantially.

Our present experimentally derived model for changes in BASE under ordinary and accelerated AMTEC conditions includes no crystalline phase transformation of the beta" alumina phase, but allows for slight soda loss from that phase. The model ascribes most changes in the performance of BASE to loss of excess soda present as  $\text{NaAlO}_2$  at grain boundaries, with a maximum mass loss of about 0.5% of the BASE mass. The BASE ceramic usually contains about 1% of the  $\text{NaAlO}_2$  phase, due to the requirements of the liquid sintering process used to fabricate dense BASE ceramic.

We have recently reported that BASE with RhW electrodes in an SETC experiment in which the hot BASE is protected from metal evaporating from the stainless steel vacuum chamber by a niobium 1%zirconium shield shows no evidence of a sustained decrease in conductivity at 1173K over 2500 hours. ( Williams, 1999) Furthermore, in the same experiment, there was no sustained drop in the exchange current of the RhW electrode/ BASE interface, indicating that the surface of the BASE undergoes no decomposition under these conditions. The exchange current in AMTEC cells has been discussed in previous work. (Williams, 1990a, Williams, 1990b) Earlier work in SETC experiments showed that, with shielding, little degradation in either the ionic conductivity of the BASE or the exchange current of the TiN/BASE interface is observed at 1123 and 1173K. Break-in behavior of TiN on BASE was observed in an SETC experiment at 1123K without a titanium shield, and during a test, at 1223 K in which the shield ruptured. Post-mortem results of a test with broken shield showed that Mn vapor can lead to degradation of BASE with loss of sodium, uptake of Mn by the solid electrolyte ceramic, and formation of  $\text{MnAl}_2\text{O}_4$  and  $\text{Al}_2\text{O}_3$ .

## EXPERIMENT

BASE stability in low pressure (0.1-10 Pa) sodium atmosphere was tested by measuring the electrolyte resistance of BASE in a four probe configuration during sodium exposure test cell (SETC) operating at temperatures from 1100K and 1223K for 500 to 3000 hours, and by characterizing the time dependence of the exchange current at the TiN/BASE or RhW interface with two-probe impedance measurements. (Williams 1995). SETC experiments were run with titanium, niobium 1%zirconium, and molybdenum/tantalum shields between hot stainless steel components and RhW or TiN electrodes on BASE in low pressure sodium vapor. Our investigation utilized lithium stabilized beta"-alumina ceramic from Ionotec (Britain) and Ceramtec (Utah) as well as ceramics from those manufacturers modified by pretreatment.

Sodium meta-aluminate,  $\text{NaAlO}_2$ , was prepared as the anhydrous phase by dehydration of the hydrated reagent, and was characterized by XRD . All of our tests on BASE were carried out with Ionotec or Ceramtec lithia stabilized BASE ceramics, which have near identical nominal compositions. Some of these samples were modified by annealing processes prior to experiments. The nominal composition of Ceramtec BASE is  $\text{Na}_2\text{O} (\text{Li}_2\text{O})_{0.176} (\text{Al}_2\text{O}_3)_{6.21}$  and Ionotec BASE is 99.25 weight %  $\text{Na}_2\text{O} (\text{Li}_2\text{O})_{0.176} (\text{Al}_2\text{O}_3)_{6.16}$  but includes 0.75 weight %  $\text{ZrO}_2$ . The Ceramtec BASE had a varying content of  $\text{NaAlO}_2$  near 1% but sometimes higher, while Ionotec BASE always is close to 1 weight %  $\text{NaAlO}_2$ . Mass loss, annealing, and phase change studies of BASE, modified BASE samples, and pressed pellets of sodium aluminate were carried out at several temperatures for periods of hundreds to thousands of hours either in low pressure sodium or in vacuum with zirconium getters as previously described.

## RESULTS AND DISCUSSION

After a small initial decrease in BASE conductivity, there was no systematic variation in conductivity for up to 2500 hours, for cells with RhW electrodes. However, the four probe conductivity sometimes showed abrupt decreases, followed by slow relaxation to the conductivity before the decrease. Similar transient perturbations were shown, more often, as increases in the ohmic series resistance  $R_{\text{ser}}$ , measured between pairs of electrodes, and in the width of the arcs between high and low frequency intercepts, designated as  $R_{\text{act}}$ , obtained from impedance measurements, even though there was also no systematic and continuous decrease in these parameters. Perturbations in measurements in SETC cells are occasionally caused by instrument problems or by electrical contacts developing between one or more of the leads and the vacuum chamber, which is usually at ground. These conditions were ruled

out in the cases described here, because instrumental problems effect all measurements done at the same time, and electrical contacts to ground can be ruled out with measurements with an ohmmeter.

The perturbations in the conductivity from the four probe measurement is interpreted as a resistance increase in the section of the BASE cylinder between the two innermost electrodes. Similarly, the series resistance measured in the two probe experiments has a significant but not exclusive contribution from the electrolyte resistance in the gap between the two electrodes. The separate occurrence of all three resistance increases is only consistent with localized resistance increases in the BASE itself, although other phenomena could account for each of the two probe resistance changes. We have found that BASE samples exposed to low pressure sodium gas for hundreds to thousands of hours at 1023K to 1123K appear somewhat more susceptible to fracture when stressed, compared to as-received ceramic, but we have not quantitatively measured this effect. However, microscopic examination shows no evident cracks following the tests.

Mass loss and phase change investigations showed that sodium aluminate,  $\text{NaAlO}_2$ , undergoes thermal decomposition at temperatures well below 1173K. At 1123K for 500 hours, the beta" alumina phase appears to be the major new phase formed, but some beta alumina is also formed. At 1073K for 500 hours,  $\text{NaAlO}_2$  pellets lose about 10% of their mass, but diffraction due to sodium beta" or beta alumina is not seen. It is possible that  $\text{NaAlO}_2$  may lose sodium oxide, but that the kinetics of crystallization of the beta" and beta phases are very slow at this temperature. This lends support for our model of the resistance fluctuations and, potentially, mechanical strength changes in BASE at the low pressure side under AMTEC operating conditions, at temperatures as low as 1023K to 1073K. X-ray diffraction (XRD) shows several weak peaks and shoulders in the diffraction patterns of the BASE ceramic which do not fit the beta"-alumina pattern. Some of these peaks can be assigned to very small amounts of  $\text{NaAlO}_2$ ,  $\text{Na}_2\text{CO}_3$ , alpha  $\text{Al}_2\text{O}_3$ , and  $\text{ZrO}$ , with perhaps in preferential orientation at grain boundaries, or they might be due to an unidentified phase. Both  $\text{NaAlO}_2$  and  $\text{Na}_2\text{CO}_3$  present in the ceramic may be expected to thermally decompose under AMTEC operating condition.

Our model for the abrupt local resistance increases followed by a slow return to the original resistance is that thermal decomposition of the  $\text{NaAlO}_2$  phase releases sodium and oxygen vapor resulting in void formation at grain boundaries between the crystals or the dominant beta" alumina phase. This decomposition and attendant volume decrease of the intergranular phase is driven by its thermodynamic instability at the low pressure of oxygen and sodium in our SETC cells. The same process might occur more slowly at the low pressure side of the BASE electrolyte in an AMTEC cell, and might to some degree be suppressed by maintaining a significant sodium vapor flux at all times. Thermal decomposition of  $\text{Na}_2\text{CO}_3$  would be still faster and harder to suppress than  $\text{NaAlO}_2$  decomposition, but  $\text{Na}_2\text{CO}_3$  is not specified by the manufacturers as an impurity phase and is not expected to survive the ceramic firing process; it should only be present at or near the BASE surface as a consequence of handling in air after fabrication. Recovery of the BASE sample resistance suggests that the voids formed are extremely small and close due to sintering or creep of the ceramic, which must be very slow at these temperatures. Closure of macroscopic cracks or voids is not observed in these ceramics at these temperatures. The phenomenon of local resistance increases may be related to, or accelerated by mechanical stresses on the sample, but is probably primarily driven by the thermal instability of high sodium oxide activity phases.

## CONCLUSIONS

Loss of a small amount of sodium oxide from BASE at temperatures below 1173K occurs without detectable conversion of the major phase, sodium beta" alumina to alpha alumina, but instead from decomposition of sodium aluminate,  $\text{NaAlO}_2$ , at grain boundaries. The decomposition of  $\text{NaAlO}_2$  results in transient, reversible, local changes in the solid electrolyte's ionic conductivity when the electrolyte is under stress. We have not seen evidence of a continuous conductivity or exchange current decrease, in tests at 1173K in several sodium exposure test cell experiments of several thousand hours with rhodium-tungsten electrodes.

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