

Slow Reversible and Quasi-Reversible Performance Changes in AMTEC Electrodes and Electrolytes

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ABSTRACT

This paper reports several slow reversible and quasi-reversible processes which occur in the porous electrode/solid electrolyte combination at AMTEC operating temperatures. These processes help to elucidate the evolution of the electrode and electrolyte characteristics with time. They also demonstrate that the atomic constituents of the electrode/electrolyte engage in significant dynamic motion. We report the stability of the sodium beta"-alumina phase in low pressure sodium vapor at 1173K up to 3000 hours, and the decomposition of the sodium meta-aluminate (NaAlO_2) phase present at about 1% in the BASE ceramic, which gives rise to transient local increases in the solid electrolyte resistivity due to local micro-cracking. We also report slow apparent morphological changes, possibly surface or grain boundary reconstruction, in TiN and RhW electrodes driven by changes in the local sodium activity.

INTRODUCTION

*electrochemistry
life testing*

Alkali metal thermal-to-electric converter (AMTEC) cells are under development as power sources for future robotic space missions, where they must operate for up to 15 years.[1] The porous electrode/solid electrolyte combination is critical to the alkali metal thermal-to-electric converter (AMTEC) operation. Mission duration and high temperature operation of AMTEC's, to perhaps 1150K at the sodium beta"-alumina solid electrolyte (BASE) ceramic, have driven the need to investigate potential degradation reactions under accelerated conditions. The beta"-alumina solid electrolyte (BASE) ceramic is the single component in AMTEC for which no substitution appears possible. Sodium beta"-alumina is one of the best characterized solid electrolytes, but its chemistry at temperatures from 700K to 1600K is only partly understood.[2-10] The BASE solid electrolyte is not typically phase pure sodium beta"-alumina, and contains sodium aluminate if prepared by liquid phase sintering, and may contain traces of sodium

beta-alumina as well. While several potential good AMTEC electrodes exist, it is equally important that the electrodes exhibit good performance over a long lifetime.[11-13]

At JPL, a major focus of our work has been on the slow irreversible degradation processes which may occur in electrodes and BASE, resulting in a decline in performance.[6,7, 14-17] Examples of such irreversible processes under AMTEC operating conditions include grain growth of electrode materials in Mo, TiN, and RhW electrodes; loss of volatile constituents such as sodium molybdate, and loss of sodium oxide from beta"-alumina at low sodium pressures to form either beta alumina or alpha alumina. The distinction between irreversible processes and reversible processes is of course vague, depending on time, temperature, and chemical activity parameters. Reversible and quasi-reversible processes are important because they may cause transient changes in material characteristics leading to lowered performance or failure, and also because they provide valuable information about slower irreversible processes to which they are related.

Slow reversible or quasi reversible processes which have been identified include reforming and restructuring of the adsorbed sodium surface layer on electrodes with operation changes; [18] interconversion of Na_2MoO_4 and $\text{Na}_2\text{Mo}_3\text{O}_6$ in oxidized molybdenum electrodes[14-16]; uptake (and loss) of neutral sodium defects from BASE [8]; de-adhesion and re-adhesion of electrodes from BASE as a result of temperature cycling [17]; modification of the strength of the BASE due to (1) sodium oxide loss from BASE grain boundaries and (2) creep and sintering in BASE [6,7]; and changes in electrode performance characteristics which are probably due to structural reorganization of the electrode, discussed here. In these examples, the times associated with slow processes range from several seconds to thousands of hours. By contrast, other chemical processes in AMTEC studied and characterized at JPL, which are considered to be fast occur in times from 10^{-12} sec (charge transfer) to 10^{-6} to 10^{-3} sec (free molecular flow of sodium atoms through thin electrodes and double layer charging).

EXPERIMENTAL

The measurements of the ionic conductivity and the apparent charge transfer resistance (R_{act}) were carried out in a sodium exposure test cell (SETC) which has been previously described in detail.[19] Briefly, the SETC is an evacuated chamber containing a small quantity of liquid sodium and low pressure sodium gas, as well as one or more BASE electrolytes, each with four electrodes permitting a variety of electrochemical measurements. All the electrodes are wrapped with a Mo or a rhodium coated Mo electrode grid, which is tied down with 0.38 mm diameter Mo wire. The ceramic between the electrodes is not wrapped or tied, and therefore the compressive stress on the ceramic tube is non-uniform.

This paper will discuss results obtained primarily from two SETC experiments each of which used two BASE sections with electrodes, but will briefly discuss earlier experiments also. One of the SETC experiments was operated for 1500 hours at 1173K, with sputtered and chemically fabricated TiN electrodes, and used a titanium liner to protect the experiment from volatile constituents of the stainless steel vacuum chamber.[17] The second SETC experiment was operated for 3000 hours at 1173K, with electrodes of approximate composition $Rh_{1.5}W$ and $Rh_{2.5}W$, deposited by co-sputtering from elemental targets. It utilized an e-beam welded Nb-1%Zr liner to prevent contamination of the experiment. Electrochemical techniques included electrochemical impedance spectroscopy (EIS) to very low frequencies, and square wave and cyclic voltammetry. Responses to these measurements were monitored approximately daily over the course of the experiments.

Mass loss and crystalline phase change experiments have been carried out at 1273K on pressed pellets and sintered pieces of sodium aluminate, $NaAlO_2$, in vacuum with zirconium getters as previously described. Sodium meta-aluminate was prepared as the anhydrous phase by dehydration of the hydrated reagent.

All of our tests on BASE were carried out with Ionotec or Ceramtec lithia stabilized BASE ceramics, which have near identical compositions. The nominal composition of Ceramtec BASE is $Na_2O (Li_2O)_{0.176} (Al_2O_3)_{6.21}$ and Ionotec BASE is 99.25 Weight % $Na_2O (Li_2O)_{0.176} (Al_2O_3)_{6.16}$ but includes 0.75 weight % ZrO_2 . The Ceramtec BASE had a varying content of $NaAlO_2$ near 1% but sometimes higher, while Ionotec BASE always is close to 1 weight % $NaAlO_2$. [20]

RESULTS AND DISCUSSION

The results of ionic conductivity measurements of two Ionotec BASE ceramics with four sputter-deposited rhodium-tungsten electrodes are shown in Figures 1 and 2. The first tube shows an anomalously large increase in measured electrolyte resistivity at about 1900 hours, with slow recovery to higher conductivity following. The apparent charge transfer resistances of the four pairs of rhodium-tungsten electrodes are also shown in Figures 1 and 2. The apparent charge transfer resistance is largely reciprocal to the exchange current, but has small contributions from the ionic resistance of the electrolyte immediately underneath the electrode, and from sodium

gas transfer through the electrode. All four pairs show an initial decline, but the 7-8 pair spikes to high resistance after about 200 hours, slowly recovers, and repeats this phenomenon twice later in the experiment. The 2-3 pair shows a major spike in R_{ser} at about 1900 hours, which correlates well with the anomaly in the four probe ionic conductivity data on the same BASE tube at this time. The only anomaly in the ionic conductivity measurement correlates fairly well with the anomaly in R_{act} of the 2-3, but the R_{act} anomaly precedes the R_{ser} and resistivity anomaly, and R_{act} anomalies occur without significant deviation in the ionic conductivity. Two of the three major anomalies observed for the 7-8 pair of electrodes are also present in the series resistance, which is equal to the high frequency intercept in EIS, as shown in Figures 1 and 2. The TiN experiment, and several other previous SETC experiments, have also shown jumps in resistance of some electrode pairs, but recovery was not monitored as thoroughly in those experiments. Our hypothesis is that the uneven compressive stress on the ceramic, coupled with slow loss of material, gives rise to micro-cracks in the ceramic which increase its resistance, probably result in local weakening, but heal slowly with further heating. We call these micro-cracks, as the gaps introduced to the ceramic must be very narrow, possibly little more than 1.0 nm, and are probably localized at certain grain boundaries. However, a collection of associated micro-cracks may extend through the ceramic for a significant distance, especially if it forms as a result of an applied stress. Since we have observed only very slight mass loss in ceramics comprised of about 99% sodium beta" alumina, we attempted to determine if a minor phase might be responsible for the phenomenon.

The mass loss observed for samples of sodium meta-aluminate, $NaAlO_2$, heated at 1273K for about 500 hours was 16% for a pressed pellet sample. X-ray diffraction analysis indicated that the annealed pressed pellet sample still contained a major phase with the $NaAlO_2$ crystal structure, but also contained a significant amount of sodium beta and/or beta" alumina or an intergrowth of these phases. We can further hypothesize that gradual conversion of the about 1% $NaAlO_2$ in the BASE ceramic results in slow morphology changes in the ceramic tube, which under the influence of uneven applied stress, give rise to micro-cracks for a substantial time. Loss of Na_2O and conversion of $NaAlO_2$ to beta or beta" alumina, may continue to occur long after applied stresses on the ceramic have disappeared.

The results of square-wave potential experiments on RhW and TiN electrodes in SETCs are shown in Figure 3. Gradual changes in performance continue for periods of minutes to hours after a change in the applied potential, which results in a change in ambient sodium activity. These slow changes can result in either improvement or degradation of up to about 20% of the instantaneous performance of the electrode. They also correlate well with minor, low-frequency features in the impedance spectra of the same electrodes, measured to typically 0.001 Hz. In the SETC experiments, we switched the cells' polarity, so such large changes would not be expected in an operating AMTEC. These processes are significantly slower than charging the interface between electrode and electrolytes, which occurs on the order of 10^{-3} seconds, or modifying the adsorbed sodium layer throughout the porous electrode, which should occur within several seconds. They are comparable to the slow changes in oxidized Mo electrodes, in which $Na_2Mo_3O_6$ and Na_2MoO_4 are

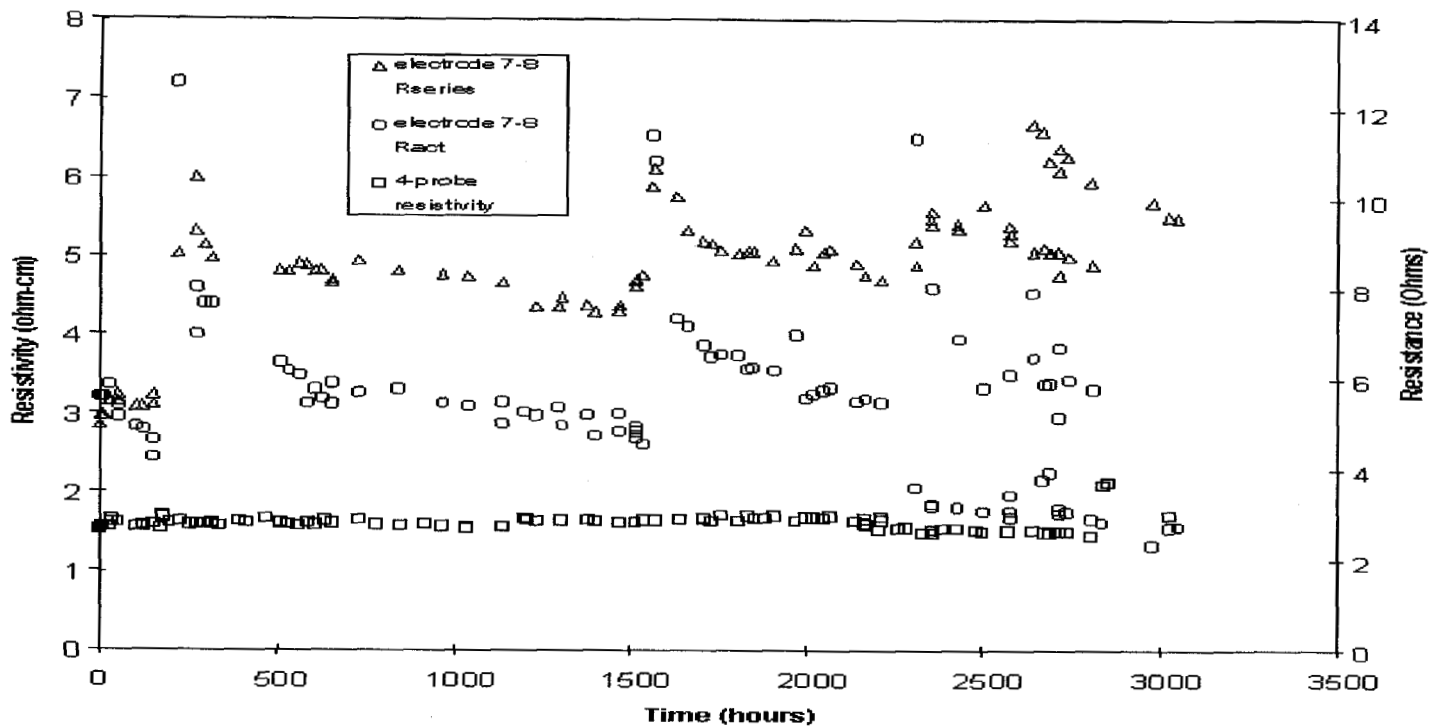


Figure 1. The four probe resistivity and Rser and Ract for the 7-8 electrode pair in the Rh_{2.5}W SETC experiment. The four probe resistivity is measured between the 6 and 7 electrodes in this experiment.

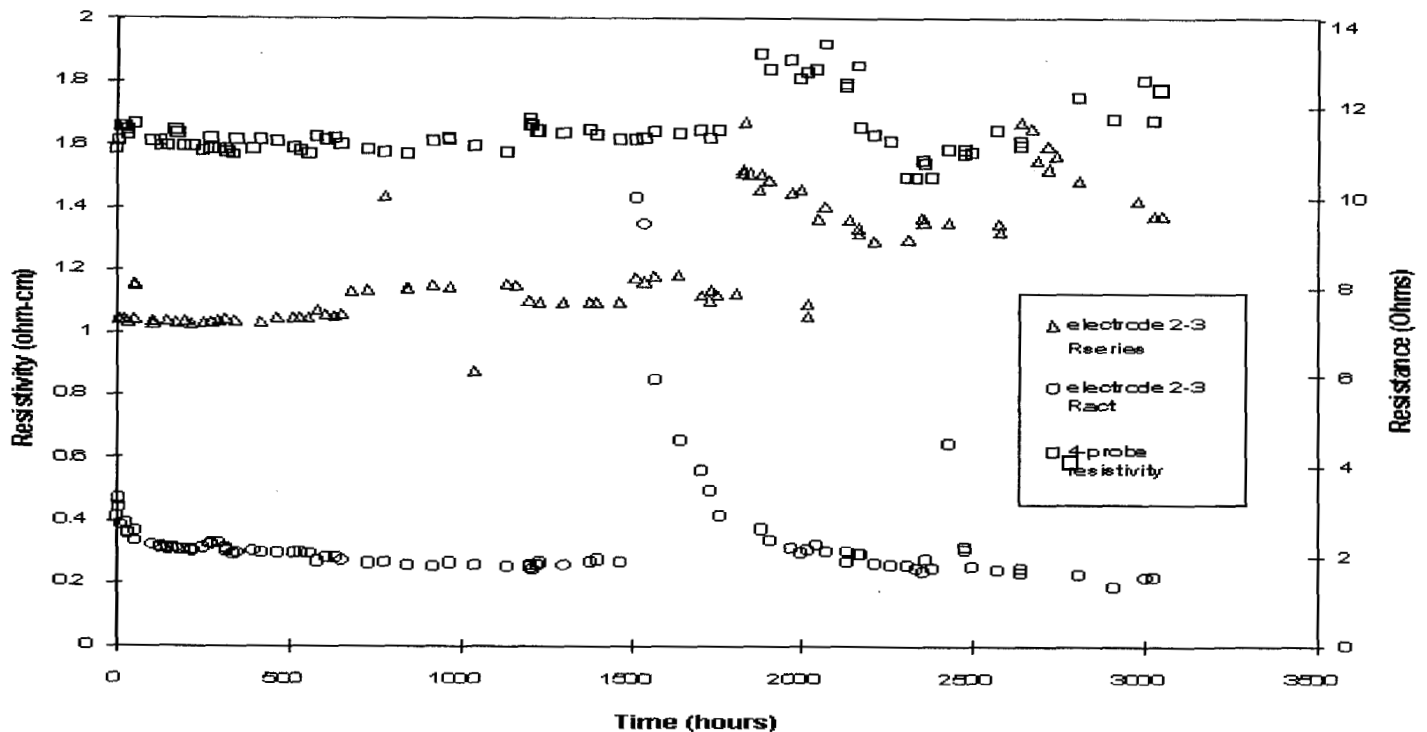


Figure 2. The four probe resistivity and Rser and Ract for the 2-3 electrode pair in the Rh_{1.5}W SETC experiment. The four probe resistivity is measured between the 2 and 3 electrodes in this experiment, and correlates well with the Rser measured for these electrodes. The increase in Ract for the 2-3 pair precedes the increase in Rser and the resistivity, suggesting that a microcrack started in the BASE underneath the 2 or 3 electrodes, and propagated into the gap between them.

interconverted on a time scale of many minutes, but these processes in TiN and RhW electrodes persist after operation at temperatures and durations which would preclude the presence of Na_2MoO_4 or Na_2WO_4 . We hypothesize that the sodium adsorption layer first responds to the potential change, and then the underlying refractory surface characteristics are modified as a result, requiring movement of some of the atoms making up the refractory electrode surface. For some electrodes, this suggests that prolonged operation under constant conditions may result in minor performance improvements. Observation of this process over long life tests also provides us with another probe of the overall electrode morphology evolution. Nothing in the observation of this phenomenon alone indicates any new degradation mechanism, but observing these changes may be valuable in probing electrode grain growth and indicating means to improve electrode performance.

CONCLUSIONS

This information is useful to both mechanistic studies undertaken to improve electrode performance, and life studies where failure may be due either to an irreversible or a transient condition. Operation of BASE electrolyte for 3000 hour at 1173K in about 10-100 Pa sodium vapor with tungsten rhodium electrodes and a niobium-1% zirconium liner in the test cell shows no systematic change characteristic of degradation of the sodium beta^{II}-alumina phase or major deleterious change in the electrode material, which showed net improvement from initiation to termination of the experiment. Some abrupt increases in resistance followed by slow return to pre-event values indicate micro-cracking followed by healing in the BASE ceramic. Mass loss experiments show that while the BASE ceramic loses little mass, 0.1%, over

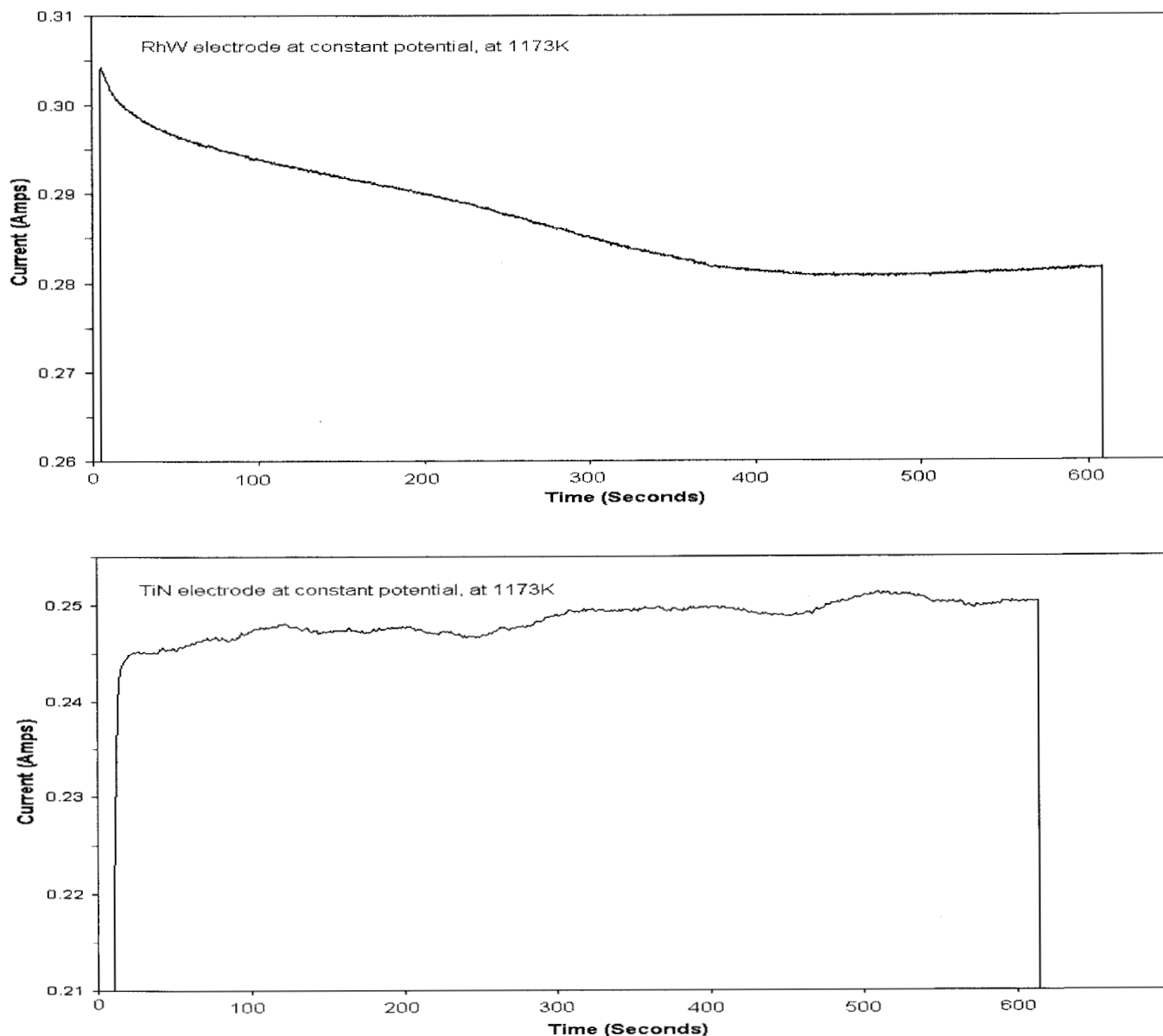


Figure 3. Current at RhW and TiN electrodes following a step to +3.0V from 0.0 Volts, in SETC experiment, at 1173K, after operation of SETC for 1700 hours.

500 hours in vacuum at 1273K, sodium meta-aluminate under identical conditions loses about 16% of its mass and is partly converted to the beta and/or beta"-alumina phases. We conclude that the presence of NaAlO₂, a minor phase presumed to be present at the grain boundaries in liquid sintered BASE, is less thermally stable under AMTEC operating conditions than is the sodium beta" alumina majority phase. Some very minor loss of sodium oxide from BASE without phase transformation, or phase transformation of BASE over extremely long times, cannot yet be ruled out. The first product of a very slow phase transformation would be expected to be beta alumina, which we have not observed so far below 1273K, and some formation of the conducting beta alumina phase would be tolerable in AMTEC devices.

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