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ADVANCES IN HIGH TEMPERATURE COMPONENTS FOR AMTEC (ALKALI METAL THERMAL-TO-ELECTRIC CONVERTER

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ABSTRACT

Long lifetimes are required for AMTEC (or sodium heat engine) components for aerospace and terrestrial applications, and the high heat input temperature as well as the alkali metal liquid and vapor environment places unusual demands on the materials used to construct AMTEC devices. In addition, it is important to maximize device efficiency and power density, while maintaining a long life capability. In addition to the electrode, which must provide both efficient electrode kinetics, transport of the alkali metal, and low electrical resistance, other high temperature components of the cell face equally demanding requirements. The beta" alumina solid electrolyte (BASE), the seal between the BASE ceramic and its metallic transition to the hot alkali metal (liquid or vapor) source, and metallic components of the device are exposed to hot liquid alkali metal. Modification of AMTEC components may also be useful in optimizing the device for particular operating conditions. In particular, a potassium AMTEC may be expected to operate more efficiently at lower temperatures.

INTRODUCTION

The basic performance of AMTEC cells is well understood, and quantitative modelling of the performance of some electrode has been carried out.[1-3] Long life performance is now the critical issue for AMTEC device development. Tests have been carried out to evaluate the high temperature performance of critical AMTEC components. This paper will not discuss "cold-side" component performance, nor will it discuss current collection grids, which are discussed in detail in several other papers. It will discuss progress made in understanding the relative performance of AMTEC components such as electrodes, electrolytes, working fluids, and seals as device operating temperature is varied. Most metallic components are especially subject to corrosion in hot liquid alkali metals containing dissolved oxides. Stability issues of AMTEC components may be addressed by life testing, accelerated testing, and modelling based on known kinetic and thermochemical data. Electrodes are now available which may be projected to perform well for many thousands of hours, on the basis of observed sintering rates under actual or simulated AMTEC

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operating conditions. These include refractory alloys of tungsten with platinum or rhodium, and refractory, conducting transition metal/ metalloid compounds such as TiN and ZrN, and, at slightly lower temperatures, thin Mo electrodes. [4-6]

A potentially significant modification of the AMTEC device is substitution of the usual working fluid, sodium, with potassium, which is the only metal which may give improved performance characteristics in a beta"-alumina ceramic based thermal to electric conversion device. Potassium has the potential to provide high power densities to a lowest practical heat input temperatures of about 800K, but the properties of potassium BASE have not been as well studied as those of sodium BASE. The required properties of the electrolyte are not limited to good conductivity, but stability and compatibility with other components are also necessary. In particular, while both Na-BASE and K-BASE are known to be thermodynamically stable phases under some conditions, it is not known if decomposition reactions occur more rapidly for the potassium phase in contact with liquid K, and if the lower projected operating temperature will result in an overall greater device lifetime.

THE AMTEC WORKING FLUID

Replacement of sodium in a liquid metal thermal to electric converter may be considered as a potential means of attaining good performance characteristics under different operating conditions. The requirements for a liquid metal to function as a competitive working fluid, compared with sodium, in a electrochemical thermal to electric converter, include a vapor pressure greater than, or comparable to, that of sodium over the device's operating temperature range; a high ionic conductivity as a cation in a solid electrolyte thermodynamically stable to the liquid metal working fluid and its vapor, and mechanically robust under the operating conditions of the cell; a melting point low enough to be convenient for use with the device's condenser temperature range. Potassium is the only reasonable candidate at this time, although other liquid metals might be considered if ionic conductors stable over a wide enough temperature range or having high enough conductivity were available. Potassium's vapor pressure varies from 2-6 times that of sodium over the AMTEC operating temperature range.[7-10] The conductivities of the ß" phase single crystals are just slightly lower than those of Na ß" at high temperature.[11,12] K-ß"-alumina is stable in the temperature range in which AMTECs are likely to operated; ceramics can be fabricated from this material and have demonstrated mechanical properties similar to those of the sodium analog.[13]

Transport through electrodes by free molecular flow and collision rate dominated electrode kinetics would be slower for K than for Na by a factor equal to the ratio of the square-roots of their atomic masses.[2,14] In electrodes in which alkali transport is dominated by surface diffusion, potassium may offer substantial improvements compared with sodium. Reported values for the surface diffusion of potassium on tungsten are in general higher than for sodium on tungsten under

equivalent conditions, although there is variation among reported values.[15,16]

ELECTROLYTE PROPERTIES

Previous results on single crystals have shown that K^+ ß"-alumina (K-BASE) is a better ionic conductor than Na^+ ß"-alumina (Na-BASE) at lower temperatures, and that their conductivities are almost identical at the highest temperature at which measurements were made.[11,12] On the other hand, K-BASE ceramics were about ten times lower in conductivity than Na-BASE ceramics, although the conductivity ratio improved with increasing temperature, and both ceramics contained some ß phase contaminating the ß" phase.[13]

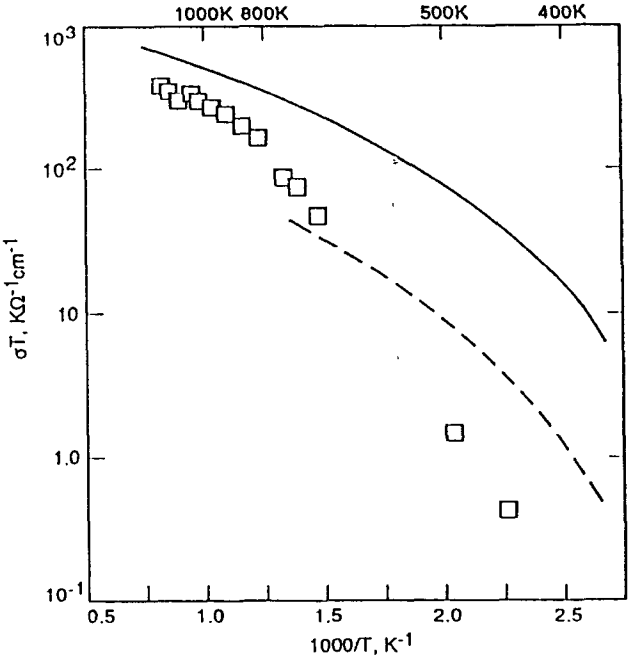

Figure 1. The variation in ionic conductivity vs. temperature for K-BASE and Na-BASE ceramic. The squares are results of this work for K-BASE, while the solid curve is from Cole, Weber and Hunt for Na-BASE, and the dashed curve is the dependence for K-BASE from Crosbie and Tennenhouse.

We have prepared K-BASE ceramic samples using a modified version of the exchange reaction with KCl reported by Crosbie and Tennenhouse, and have measured the conductivity, by determination of both d.c. current voltage curves and a.c. impedance in a four probe configuration in K vapor at temperatures up to 1223K, using the method of Cole, Weber, and Hunt.[13,16] The K vapor was maintained at a low but significant level through control of the end flange condenser temperature at up to 500K. The results are shown in Figure 1, along with a plot of the conductivity of Na-BASE ceramic and earlier data on K-BASE measured in a liquid K cell, from the work cited.[6,10]

ELECTRODE PERFORMANCE WITH TEMPERATURE

The transport properties of thin molybdenum electrodes and the more advanced and refractory alloys, WPt_2 and WRh_2, are very much different under d.c. operation.[6] As described in a previous publication, the electrodes' transport may be described by a dimensionless morphology parameter, and may be related to an overall diffusion coefficient for the electrode, or a surface diffusion coefficient in the case of WPt_2 and WRh_2, if the electrodes' morphologies can be quantitatively described.[2]

The diffusion coefficients for thin Mo electrodes, from a large number of AMTEC electrode test cell experiments, and WRh_2 electrodes, measured in a sodium

vapor cell, are shown in Figure 2. The Mo temperature dependence is primarily due to the $T^{0.5}$ dependence of free molecular flow pressure drops. [2,14] The WRh_2 electrodes show activated transport with an activation energy of 48 kJ/mole, and a pre-exponential factor of D_0=153 cm^2s^{-1} . The deviation from linearity at low temperature is due to the contribution of free molecular flow diffusion in these relatively non-porous electrodes, which becomes more important as surface diffusion becomes slower.

Free molecular flow alone in the WRh_2 electrodes is expected to produce a pressure gradient from 10 to 20 times that of the very porous thin Mo electrodes. Correcting for the surface area and roughness within the cracks in the WRh_2 electrodes, the pre-exponential for surface diffusion of Na on WRh_2 is calculated to be about 20 to 100 cm^2s^{-1}, if surface diffusion is the activated transport mechanism, based on crude calculations from electrode morphologies observed by scanning electron microscopy. Surface diffusion on WRh_2 may be on the order of a hundred times faster than Na diffusion on W at these temperatures, due to the large difference in the pre-exponential terms. If grain boundary diffusion contributes, the pre-exponential part of the diffusion coefficients would be much smaller since the grain boundary area available for transport would be many times larger than the surface area of cracks in the electrode; however the overall activated transport is still much faster than on W or Mo electrodes.

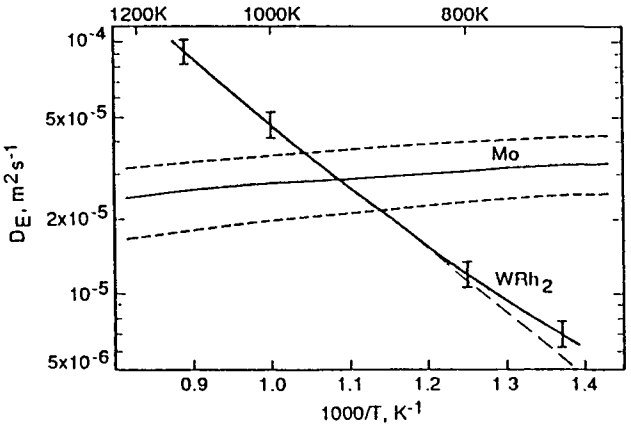

Figure 2. The diffusion coefficients for 0.5-0.7μm Mo and 1.0-1.2 μm WRh_2 AMTEC electrodes.

BASE TO METAL SEALS

Two approaches to BASE to metal seals are being investigated at JPL. The first is a close tolerance seal between niobium or tantalum and BASE using TiCuNi Brazing alloy. The second approach is pre-metallization of the BASE tube via sputtering with a thin layer of active metal alloy, followed by brazing with a more conventional braze alloy using a good vacuum. The first technique has produced seals which can reliably operate for at least 1000 hours, but thicker layers of TiCuNi braze filler tend to develop grain boundary cracks on cooling, due to thermal expansion mismatch. These cracks may close on heating if the leak rate is not large, and thinner layers seem not to develop leaks. The second approach has produced strong bonds, but optimization to produce hermetic seals has not been completed.

MATERIALS COMPATIBILITY

A critical issue effecting the development of AMTEC devices is the stability of metal components to hot liquid sodium. This issue

is common to many thermal to electric converters, but in the case of AMTEC a crucial technical question is the degree to which dissolved sodium oxide in sodium in an operating AMTEC may be maintained at as low a level as possible. Most metals are much more readily dissolved in sodium oxide contaminated Na_l. The interaction of BASE with Na_l over extended periods is therefore of great concern, since ideally there should neither be oxygen loss from the BASE nor a significant quantity of dissolved oxygen in the hot Na_l. Slow dissolution rates of metals in O-free Na_l is also a critical issue.

CONCLUSIONS

The potential operating range for AMTEC devices may be expanded to 800-1300K by use of potassium as working fluid at lower temperatures and considering advanced designs including tube bundles and flat plate stacks. Selection of electrodes as well as working fluids will depend on the expected operating range. Materials stability and compatibility over extended periods of time remains a concern which must be addressed by testing and development of reliable life models.

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