Lifetimes of AMTEC Electrodes:
Molybdenum, Rhodium-Tungsten, and Titanium Nitride

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Abstract. The lifetime of three types of AMTEC electrodes is predicted from the rate of grain growth in the electrode. Grain size is related to electrode performance, allowing performance to be correlated with grain growth rate. The rate of growth depends on physical characteristics of each material, including the rates of surface self-diffusion and molecule mobility along grain boundaries. Grain growth rates for molybdenum, rhodium-tungsten and titanium nitride electrodes have been determined experimentally and fit to models in order to predict operating lifetimes of AMTEC electrodes. For lifetimes of 10 years or more, Rh_xW electrodes may be used at any operating temperature supportable by the electrolyte. TiN electrodes may be used in AMTEC cells only at operating temperatures under 1150 K, and Mo may be used only below 1100 K.

INTRODUCTION

AMTEC, the Alkali Metal Thermal to Electric Converter, is a direct energy conversion device capable of near-Carnot efficiencies. The device is an alkali metal concentration cell which uses a β''-alumina solid electrolyte (BASE) tube as a separator between a high pressure region containing liquid metal, generally sodium, at 900 - 1300 K and a low pressure region containing a condenser at 400 - 700 K (Weber, 1974; Cole, 1983). Single cells have performed at high power densities, with open circuit voltages up to 1.6 V and current densities up to 2.0 A/cm^2 (Williams, *et al.*, 1989). Efficiencies as high as 13-15% have been reported (Underwood, *et al.*, 1993; Sievers *et al.*, 1994).

NASA's interest in AMTEC is as the power source for outer planet exploratory spacecraft. For an AMTEC device to be feasible for either space or terrestrial applications, it must have an operating lifetime of 7 - 15 years. Tests done in AMTEC research have shown that, on the time scales studied (up to 8000 hours), the electrode is the component most likely to influence device performance and limit operating lifetime. The ideal AMTEC cathode is one which has three primary characteristics:

1. It is thin enough to allow ready transport of sodium atoms from the electrode-electrolyte interface through the electrodes to the low pressure vapor space, for vaporization and transport to the condenser;
2. It is thick enough to offer good electrical conductivity for the electrons traveling from the external circuit to the interface where recombination of electrons and sodium ions takes place; and
3. It has a lifetime which will allow continuous operation with minimal degradation in performance for seven (mission to Europa) to fifteen years (mission to Pluto).

Electrode materials tested at JPL in AMTEC and Sodium Exposure Test Cell (SETC) experiments have included refractory metal and metal alloy electrodes, including molybdenum, tungsten, rhodium-tungsten and platinum-tungsten, and titanium nitride electrodes (Wheeler, *et al.*, 1988; Williams, *et al.*, 1989; Williams, *et al.*, 1990). This paper considers the characteristics of molybdenum, rhodium-tungsten and titanium nitride electrodes, and predicts operating lifetimes of those materials as AMTEC electrodes based on data taken during several hundreds or thousands of hours of operation under AMTEC conditions.

All electrodes discussed here are considered for use as cathodes, although use as anodes is not precluded, and were sputter-deposited to thicknesses of 0.75 - 1.5 μm.

ELECTRODE LIFE MODEL

The electrode life model developed over the last several years at JPL is based on a model of grain growth and the relationship between grain radius and electrode performance. Grain radius has been correlated to the temperature independent exchange current, B, and to electrode power experimentally. Development of a model of electrode life proceeds through four steps: determination of a model of grain growth for each electrode material, development of an expression for the relationship between B and grain radius, development of an expression for the relationship between B and Power, and finally, calculation of electrode life by setting an arbitrary decline in power and relating it to grain radius through the previous two expressions.

Grain Growth Model

Lifetime characteristics of molybdenum and two preparations of Rh_xW have been previously reported (Ryan, et al., 1994). A model for grain growth based on a model of coalescence of spheres was developed and applied to Mo, RhW and Rh_2W. The grain radius was correlated with electrode performance through the temperature independent exchange current, B (Williams, et al., 1990b), and B was independently correlated with electrode power (Ryan, et al., 1994). Further data have been used to confirm the applicability of that model. The model, which is based on the Herring Law (Herring, 1950; Binh & Uzan, 1987) allows the calculation of the time, t, for two grains to coalesce into one from an initial radius R_0 as

$$t = \frac{0.89\, R_0^4}{D_S N_0 \gamma_s \Omega^2 / kT}, \tag{1}$$

where D_S is the surface self-diffusion coefficient of the electrode material, N_0 is the atom density of electrode material on the surface of the electrolyte, γ_s is the surface energy of the material, Ω is the atomic volume of the material, k is the Boltzmann constant and T is the temperature. D_S may be calculated from this expression from measured grain growth over a measured time at a single temperature. N_0 is calculated from the atomic volume as $N_0 = \Omega^{-2/3}$ (Binh & Uzan, 1987). The other factors may be, or have been, measured directly. From this equation, the final radius of a grain may be computed from the number of rounds of coalescence of spheres.

In Mo electrodes, observation of the morphology of an electrode surface led to the use of the coalescence of spheres model. After a few hundreds of hours of operation at T>1050 K, scanning electron micrographs showed a clear pattern of coalescence of Mo material into spheres (Wheeler, et al., 1988). The Herring Law model for grain growth which was used for Mo was applied to Rh_xW electrodes with success, although observation of the surface did not show that spheres were formed in the same way as in Mo. While the Herring Law model for grain growth can be used successfully to predict grain size in Rh_xW after a period of AMTEC operation, it does not fully describe the process of grain growth in that material.

Observed grain growth in titanium nitride did not follow the coalescence of spheres model, nor did application of the Herring Law model predict grain size successfully. A model based on grain boundary mobility was developed from measured grain growth of TiN in low pressure sodium vapor. The development of that model is discussed in detail elsewhere (Shields, et al., 1999). In the grain boundary mobility model, the relationship in time between the initial radius R_0 of a grain to its final radius R_f can be expressed as:

$$R_f = R_0 \left[1 + \frac{2c\gamma_s M \cos\phi\, (\exp(-E_A/RT))\, t}{R_0^n} \right]^{1/n}, \tag{2}$$

where c is a proportionality constant, γ_s is the surface energy of TiN, M is the mobility of TiN on itself, ϕ is the angle between grains, E_A is the activation energy for grain growth, R is the gas constant, and n = 3.2. To use this expression, we have used observed grain sizes grown in sodium atmosphere at known temperatures for known times in SETC experiments (Ryan, et al., 1998) and derived a value for $2c\gamma_s M\cos\phi$, which is approximately constant over the temperature range 1050-1250 K.

As neither γ_s nor M can be easily measured in our laboratory and we have not yet found these values for TiN in sodium atmosphere in the literature, we have applied the model using the derived value

$$a = 2c\gamma_s M \cos\phi \quad , \tag{3}$$

making Equation (2)

$$R_f = R_0 \left[1 + \frac{a\ [\exp(-E_A/RT)]\ t}{R_0^{\ n}} \right]^{1/n} \quad . \tag{4}$$

R_0 is measured on electron micrographs; ϕ can be taken from the same micrographs, but with less precision because photo angle is important, so it is included in a. E_A was taken from a literature value of 230 kJ/mol for the formation of TiN films by evaporation of Ti in a nitrogen atmosphere; the activation energy for grain growth may, in fact, be somewhat lower, which would result in faster grain growth. As this E_A is the same order of magnitude as was found for Rh_xW electrodes, 2.4 - 2.7 eV, this energy was used for the first order model.

The function of the proportionality constant, c, is to provide dimensional conversion factors for the dimensions of the radius to be correct. The value of n, 3.2, is taken from literature values where the grain growth characteristics of TiV and TiMn compounds were studied. The source of these values is discussed in detail elsewhere (Shields, *et al.*, 1999).

Relationship of B and Grain Radius

In studies of the grain growth rates of Mo, Pt_xW and Rh_xW electrodes, an empirical correlation between grain size and exchange current expressed as B has been developed (Ryan, *et al.*, 1994). The electrode reaction, reduction of sodium ions (Na^+), occurs at the electrode/electrolyte interface, at the perimeter of the grains. As grain size increases, total material volume is conserved and the number density of grains, and thus total contact between grain and electrolyte, decreases. B as measured in SETC experiments has been plotted as a function of observed radius R_f. The values of B calculated from experiment were fit to the expression

$$B = a - bR_f^{1/2} \quad , \tag{5}$$

where $a = 1.421 \times 10^2$ and $b = 6.218$ and R_f is expressed in nm.

This relationship between exchange current and grain radius is empirical, and is based on observed behavior of Mo, PtW and RhW electrodes. It has not yet been shown to be valid for TiN electrodes. However, it is valid to assume that exchange current will decrease as grain size increases and the length of the reaction zone decreases. The length of the TiN reaction zone may change according to a different relation than does the reaction zone in other electrode materials, but as a first order model, this approach gives an idea of the lifetime of a TiN electrode.

Relationship of Power and B

B, the exchange current, is a measure of the efficiency with which the reaction $Na^+ + e^- \rightarrow Na^0$ is carried out at the electrode/electrolyte interface. It is a sensitive probe of electrode performance, which is reflected in the overall power conversion in an AMTEC cell. A semi-empirical relationship between Power and B has been developed and previously presented (Ryan, *et al.*, 1991; Ryan, *et al.*, 1994). B can fall to ~ 50 from a starting value of 100 with only a 10% drop in power. Power drops to 70% of initial power when B drops to 20; any further decline in B results in rapid decline in power and failure of the device.

Electrode Lifetime

Electrode lifetime is the period over which electrode performance is sufficient for necessary operation device operation; from the perspective of spacecraft operation, it may be defined as the time it takes for produced power to fall to a defined level. That level is an arbitrary one; for the purposes of this discussion, times for power to fall to 90% and 70% of initial power will be presented. Using the relationship of B and Power described above, and the relationship of grain

radius and B described in Equation 5 and Figure 1, time to grow to a grain radius of 200 nm results in a power level of 90% of initial power, and a grain radius of 400 nm results in a power level of 70% of initial power.

EXPERIMENTAL

Three SETC experiments using TiN electrodes provided by AMPS, Inc. were run. The experiment has been previously described in detail (Ryan, et al., 1998). All three experiments were contained in stainless steel vacuum chambers within titanium liners to prevent volatile components of the steel from reaching the electrode and electrolyte. The sodium pool temperature was kept at 500 - 600 K. Each experiment was run at a different temperature and for a different length of time: 980 hours at 1120 K, 1850 hours at 1170 K and 500 hours at 1220 K. Current-voltage curves and two probe impedance measurements were made every 24 - 72 hours and the time evolution of the apparent charge transfer resistance R_{ACT} was plotted. The temperature independent exchange current, B, was computed from R_{ACT} (Williams, et al., 1990; Ryan, et al., 1998).

Three SETC experiments using RhW and Rh$_2$W electrodes were run at 1070 or 1120 K for 1000 to 1500 hours; the coalescence of spheres model was used to determine an expression for D_S in those preparations of Rh$_x$W. One Rh$_x$W SETC experiment using two preparations of Rh$_x$W, Rh$_{1.5}$W and Rh$_{2.5}$W was run at 1170 K for 3000 hours. Rh$_{1.5}$W data were analyzed for this paper, using a D_S which is intermediate between that for RhW and Rh$_2$W to calculate the grain radius for Rh$_{1.5}$W operated for 3000 hours at 1170 K.

Mo electrodes were operated in three AMTEC experiments which operated for periods of 100 to 300 hours at 1050 or 1170 K, and in one SETC experiment 1070 K for 500 hours. The coalescence of spheres model was used to determine an expression for D_S for Mo.

RESULTS AND DISCUSSION

Grain Radii

Grain Boundary Mobility Model - TiN The value of a, Equation 3 was derived from Equation 4 and the data from TiN experiment 1 (1120 K, 980 hours) and applied to the time and temperature data for TiN experiments 2 and 3. The value of a was derived from the model by setting $R_0 = 30$ nm, $E_A = 230$ kJ/mol, n = 3.2, T = 1120 K, and t = 980 hours as described above and finding the value that yielded a final grain radius R_f within 10% of the measured radius. a was found to be constant in the temperature range for which we have data (1120 - 1220 K). g_s and M will be temperature dependent, but relatively weakly compared with the value of $(exp(-E_A/RT))$. The value of f will be weakly time dependent, but it has been kept constant for the present purposes. The value computed is $a = 7.0 \times 10^{13}$. Using the same value of a, final grain radius calculated for other conditions correlated well with measured values:

TABLE 1. Calculated and Experimental Grain Radii for Three SETC Experiments with TiN Electrodes.

R_0 (nm)	T (K)	time (hours)	R_f calc (nm)	R_f exp (nm)
30	1120	980	82	88
30	1170	1850	138	127
30	1220	500	124	117

Coalescence of Spheres Model - Mo and Rh$_{1.5}$W The grain size of Rh$_{1.5}$W was measured after 3000 hours of operation and compared with grain size computed for this temperature and time according to the model previously presented (Ryan, et al., 1994). New Mo experiments were not run.

TABLE 2. Surface Self Diffusion Coefficients for Mo and Rh_xW in Na Vapor.

|	E_A (eV)	A (cm^2/sec)	T (K)
Mo	8.44	3.0×10^{26}	1050-1200
RhW	2.70	2.2×10^{-3}	1050-1200
Rh_2W	2.14	1.3×10^{-5}	1050-1200

The surface self diffusion coefficient can be expressed as $D_S = A \exp(-E_A/kT)$. The values derived are shown in Table 2. In the new experiment of $Rh_{1.5}W$, the measured grain radius after 3000 hours at 1170 K is 60 nm; the calculated grain radius is 55 nm, in good agreement with the observed size. According to Equation (5), B at this grain radius should be ~ 95. During the 3000 hour SETC experiment, the measured B for $Rh_{1.5}W$ electrodes was ~ 100.

Electrode Lifetime

Electrode lifetimes for Mo, TiN and $Rh_{1.5}W$ electrodes are shown in Figures 1 and 2 as functions of operating temperature. Starting grain radius, R_0, for Mo is 10 nm, for $Rh_{1.5}W$ is 5 nm and for for TiN is 30 nm. All are measured from electron micrographs of the as-sputtered material. Figure 2a shows time for grains to grow to a radius of 200 nm, resulting in a power decline of 10%, $P = .9P_i$. Figure 2b shows time for grains to grow to a radius of 400 nm, resulting in a power decline of 30%, $P = .7P_i$. For all electrodes, the initial value of B has been assumed to be 100. JPL experiments have consistently shown the initial value of B in TiN to be about 60-70% of that of Rh_xW. If the initial value of B for TiN is assumed to be 60, the lifetime will be as shown in Figure 2.
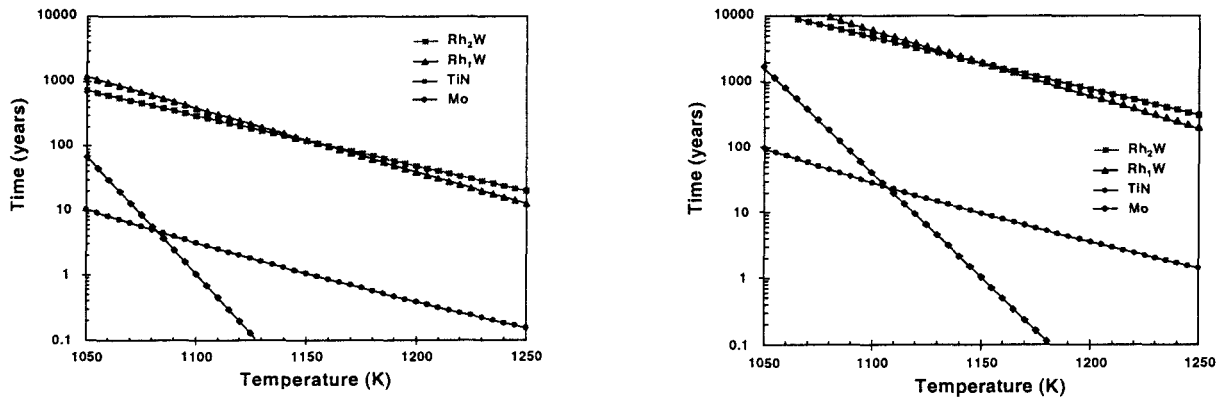
FIGURE 1. (a) Time for Mo, TiN and Rh_xW electrodes to grow to a grain radius of 200 nm, corresponding to B ~ 50 and P = .9P_i; (b) Time for Mo, TiN and Rh_xW electrodes to grow to a grain radius of 400 nm, corresponding to B ~ 20 and P = .7P_i.
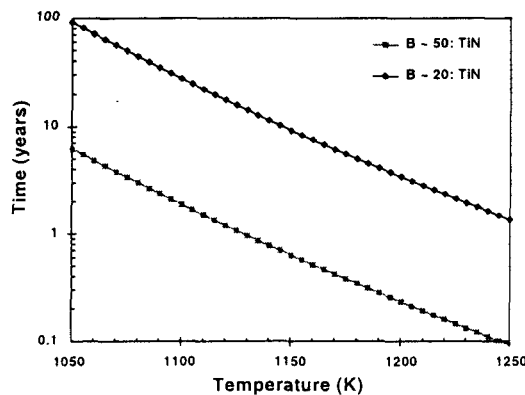
FIGURE 2. Time for TiN grain growth to result in a decline in exchange current to B ~ 50 (squares) and B ~ 20 (diamonds), assuming the initial B is 60.

CONCLUSION

Using models of grain growth developed for TiN and for Rh_xW and data taken in SETC experiments, we have predicted the lifetime of AMTEC electrodes made with those materials. With an operating temperature of 1125 K, Rh_xW electrodes will not decline appreciably in the 15 year lifetime required for an outer planet mission. As can be seen in Figure 2, Rh_xW electrodes are predicted to fall to 90% of initial power in ~100 years if there are no degradation mechanisms other than grain growth in the electrode. In contrast, Mo cannot be operated at more that 70% of initial power at 1125 K for more than a few weeks. The maximum temperature at which Mo can be operated to preserve a power of more than 90% of initial power for ten years is 1075 K. TiN is predicted to decline to 90% of initial power in ~2 years and to 70% of initial power in ~16 years. The predicted lifetime for TiN is based on a grain growth model developed for that material and the relationships among grain radius, exchange current and power density observed in other electrode materials. Experiments to confirm the applicability of the grain boundary mobility model of TiN growth are underway. The predicted lifetime for TiN must be validated with further experiments in which exchange current is correlated with both grain size and power density in the electrode.

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REFERENCES

Binh, V.T. and R. Uzan, "Tip Shape Evolution: Capillarity-Induced Matter Transport by Surface Diffusion," *Surface Science*, **179**, 540-543 (1987).

Cole, T., "Thermoelectric Energy Conversion with Solid Electrolytes," *Science*, **221**, 915-920 (1983).

Herring, C., "Effect of Change of Scale on Sintering Phenomena," *J. Appl. Physics*, **21**,301-306 (1950).

Ryan, M.A., B. Jeffries-Nakamura, D. O'Conner, M.L. Underwood, and R.M. Williams, "AMTEC Electrode Morphology Changes as Studied by Electrochemical Impedance Spectroscopy and Other Techniques," *Proc. Symposium on High Temperature Electrode Materials*, D.D. Macdonald and A.C. Khandkar, eds., The Electrochemical Society, **91-6**, 115-120 (1991).

Ryan, M.A., A. Kisor, R.M. Williams, B. Jeffries-Nakamura, and D. O'Connor, "Lifetimes of Thin Film AMTEC Electrodes," *Proc. 29th IECEC*, American Institute of Aeronautics and Astronautics, **2**: 877-880 (1994).

Ryan, M.A, R.M. Williams, L. Lara, R.H. Cortez, M.L. Homer, V.B. Shields, J. Miller, and K.S. Manatt, "The Sodium Exposure Test Cell To Determine Operating Parameters For AMTEC Electrochemical Cells", *Proc. 33rd IECEC,* American Nuclear Society, I335 (1998).

Shields, V.B., R.M. Williams, M.A. Ryan, and M.L. Homer, "Model for Grain Growth in AMTEC Electrodes" *Proceedings of 34th IECEC*, SAE, 2703 (1999).

Sievers R.K., T.K. Hunt, D.A. Butkiewicz *et al.* "Prototype AMTEC Cell Development," *Proceedings of 29th IECEC*, American Institute of Aeronautics and Astronautics, **2**, 894-898 (1994).

Underwood M.L., R.M. Williams, M.A. Ryan, B. Jeffries-Nakamura, D. O'Connor, "Recent Advances in AMTEC Recirculating Test Cell Performance," *Proc. of 10th Symp. on Space Nuclear Power*, M.S. El-Ghenk and M.D. Hoover, eds., American Institute of Physics, 885-889 (1993).

Weber, N., "A Thermoelectric Device Based on β"-Alumina Solid Electrolyte," *Energy Conv.*, **14**, 1-8 (1974).

Wheeler B.L., R.M. Williams, B. Jeffries-Nakamura, J.L. Lamb, M.E. Loveland, C.P. Bankston and T. Cole, "Performance and Impedance Studies of Thin, Porous Molybdenmum and Tungsten Electrodes for the Alkali Metal Thermoelectric Converter," *J. Appl. Electrochem.*, **18**, 410-415 (1988).

Williams, R.M., B. Jeffries-Nakamura, M.L. Underwood, B.L. Wheeler, M.E. Loveland, S.J. Kikkert, J.L. Lamb, T. Cole, J.T. Kummer and C.P. Bankston, "High Power Density Performance of WPt and WRh Electrodes in the Alkali Metal Thermoelectric Converter," *J. Electrochem. Soc.*, **136**, 893-894 (1989).

Williams, R.M., B. Jeffries-Nakamura, M.L. Underwood, C.P. Bankston and J.T. Kummer, "Kinetics and Transport at AMTEC Electrodes II. Temperature Dependence of the Interfacial Impedance of $Na_{(g)}$/Porous Mo/Na-β" Alumina," *J. Electrochem. Soc.*, **137**, 1716-1722 (1990).