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The Grain Size Effect on Thermo-chemical Properties of AMTEC electrodes

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The lifetime of alkali metal thermal to electric converter (AMTEC) is desired to last for a long time, 15 years or more, which depends primarily on thermo-electro-chemical character of electrode materials used. This study aims at the performance of electrodes by looking into their material properties mainly pertaining to the grain growth with respect to time in the grain mobility model. The electrode material studied in this work is Moybdenum. If the grain size of the electrode material reaches a certain dimension, about 500 nm, the power output starts degrading fast. It is found that Moybdenum electrodes have least power degradation for AMTEC designed for operation at the lower side of temperature, less than 1100 K as its grain growth becomes too rapid when operated above 1100 K.

Keywords: Electrode, Long life, Power degradation, Time- and temperature-dependence

1. INTRODUCTION

A thermally regenerative electrochemical device for the conversion of heat into electricity has been in demand for both terrestrial and space purposes. The alkali metal thermal electric converter (AMTEC) is a device, which has high efficiency relative to other conventional thermal to electric converters., It works between temperatures around 600 K and 1100 K at its condenser and hot sides respectively. A liquid metal (in this case we consider liquid sodium) passes from the condenser through a wick to an evaporator, where it is converted to vapor on supply of heat from some external source. The sodium vapor enters a beta" alumina solid electrolyte (BASE). The BASE tubes are connected in an electrical series. The cathode electrode is applied on the outer surface of the BASE tube by chemical vapor deposition or sputtering techniques. The anode electrode is applied to the inner surface of the BASE tube by the Weber process and is covered with molybdenum mesh current collectors in order to prevent internal electric losses [1].

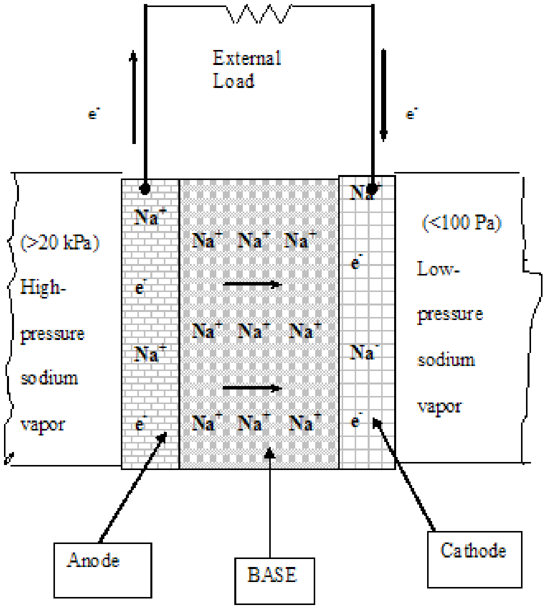

Figure 1. Schematic diagram of the AMTEC Cycle

AMTEC does not have any moving parts [2-5] except for the sodium, which flows in a closed cycle as a working fluid. The BASE is the ionic conductor and divides the AMTEC into two regions; a hot region filled with sodium at high-pressures (10-100 k Pa) and high-temperatures (900-1300 K) and a cold region at low-pressures (<100 Pa) and low-temperatures (400-700 K) [6]. The Figure 1 shows the working principle of AMTEC. A porous metal electrode (cathode) covers the low-pressure (outer) side of the BASE. The anode surface covers the inner side of the BASE at the high pressure-temperature region of the cell. Both electrodes provide a conduction path for the electrons to and from the external load. As sodium enters the hot region of the cell, due to the thermodynamic potential across the BASE, ionization of sodium metal occurs at the hot region of anode and BASE interface [7]. The sodium ions are diffused through the BASE to the cathode due to the pressure differential across the BASE. The electrons circulate through the external load producing electrical work and then reach the cathode surface where they recombine with the sodium ions at the interface between the BASE and cathode. The neutralized sodium leaves the porous electrode, moves through the vapor space, and releases its heat of condensation on the condenser surface. Nearly the entire temperature drop occurs in this low-pressure vapor space. The condensed liquid sodium moves to the wick annulus to the inlet of a small dc electromagnetic pump or a porous capillary wick, which is used to return the sodium to the high-pressure evaporator region.

2. ELECTRODE CHARACTERISTICS

The electrode performance greatly depends on its material [8]. The electrical resistance, thermal expansion coefficient, vapor pressure, and surface self-diffusion coefficients are the most desired parameters in selection for the material for electrode construction. The electrodes must have suitable properties and be stable under operating temperatures for desired period of time. They should be able to provide a site for the thermo-electro-chemical reactions for sodium ionization and recombination of sodium ions and electrons. For that we expect them to have some prerequisite characteristics such as:

1. The electrode material in contact with the BASE material should have a high tolerance to thermal expansion. Ceramic electrodes have a lower tolerance compared to the metal electrodes.
2. The negative Gibbs free energy should be large enough to prevent material loss due to dissociation
3. The electrode should be thermo-electro-chemically compatible with the BASE and other components, to prevent corrosion.
4. The sodium ions should be able to easily migrate from the high-pressure anode side to the low-pressure cathode side.
5. The electrode should not be a barrier to the sodium ions.
6. The electrons should be able to leave the anode site with least resistance and travel rapidly to the load and recombine at the cathode to complete the circuit.
7. The electrical conductivity of electrodes should be high enough to allow the electrons to move through the external circuit.
8. The electrical resistance and the surface self-diffusion should be low for an ideal electrode
9. Electrode materials should have high melting point to allow a lower surface diffusion coefficient. This aspect corresponds to low sintering of the electrode grains.
10. It is important that the electrode does not alter its physical morphology during the long hours of operation.
11. The grain of the electrode should coalesce very slowly in order to prevent voids from appearing. The electrical conductivity decreases as the voids open up [9].

The triple phase boundary involves the electrode, BASE, and sodium interaction where a longer triple phase boundary is the result of a finer grain size [10]. Also the charge transfer process occurs at the triple phase boundary. If the length of the triple phase boundary increases, the over-voltage decreases. Then the electrode with a finer grain size will obtain higher current densities.

3. THE GRAIN GROWTH OF ELECTRODE MATERIALS

The electrode lifetime is defined as the time for which the performance of the electrode is satisfactory to produce adequate power output for the AMTEC system. If the electrode grains grow to a diameter of 1000 nm (some limit to 500 nm) then they cease to function properly [11]. The sintering rate of the electrode material is a function of the operating temperature of the hot side of the cell thus the operable lifetime of an AMTEC electrode is temperature-dependent. With an increase in sintering, grain size increases, which eventually leads to a decrease in the number of grains. Therefore, contact between electrolyte and electrode also reduces. With the increase of grain size, voids within the electrode become larger which causes the electrode conductivity to decrease. Eventually, these voids grow to a huge size so that there will be no apparent grain-to-grain conduction and the effective lifetime of electrode will reach its end ultimately. In brief when the electrodes are exposed to sodium under high pressure and temperature they tend to sinter, thus affecting the porosity, resistance, the nature of grains and the contact of electrodes with the BASE. Voids or porous holes in the electrodes are formed, which allows the sodium to flow through them easily. The voids will increase after an extended period of time. This reduces the grain-to-grain contact, dropping the electrical conductivity, and ultimately disables the electrodes to function any further

4. THE GRAIN GROWTH MODEL

The thermo-chemical role played by electrodes needs to be determined in order to understand the time-dependent behavior of AMTEC. The time- and temperature-dependent behavior of electrode is highly correlated to the grain growth function of its material. Alternatively, one can calculate the grain size dependence upon time by applying the grain boundary mobility growth model to the electrode materials and thus obtain the power output of electrodes,

The grain growth is due mainly to the material diffusing between adjacent grains. The surface contact among the electrode grains is reduced as the grains grow and thus degrade the performance of the electrode. The neighboring grains continue to merge into each other until the surface energies related to the tension between the grains is balanced. This condition arises when the grains cannot grow any further because the other grains confine them and they rid their strained energy state by coalescing with other grains. The grain growth takes place with kinetics where the adjacent grain boundaries have a net motion with respect to each other. The pressure difference or driving force at the grain boundary is related to the velocity of the grains [12]. The pressure difference can be approximated with the average grain radius, assuming it to be a spherical drop, and the average grain boundary energy. Under such ideal conditions the grain size squared would grow as a linear function of time and boundary energy. However, in practice the actual pressure difference at the grain boundary has a more complex dependence on surface and volume energies on grain size and may also vary from material to material [12]. Thus for a relatively more practical situation the grain size is obtained [12, 13] as:

$$R_f = R_o[1 + at\exp(-E_A/RT)/R_o{}^n]^{1/n}, \tag{1}$$

where R_f is the final grain size after having operated for a period of time t at temperature T at the hot end, R_o is the grain radius at time zero, E_A, is the activation energy, R is the gas constant, n is called grain growth exponent to be determined and a is given by

$$a = 2cM_o\gamma_s\cos\phi. \tag{2}$$

Here c is the proportionality constant to give correct dimensions, γ_s is the surface energy and ϕ is the angle between two coalescing grains. The effect of altering parameter a ($2cM_o\gamma_s\cos\phi$), in the grain growth equation alters the behavior of the grain size for the materials used. From equation (1) it is seen that as *a*, increases, *R* increases also. The parameters $2c, M_o, \gamma_s, and \cos\phi$ on which parameter "*a*" depends cannot be easily measured in a laboratory setting. It is, however, observed that M_o *and* γ_s are somewhat temperature dependent but only weakly compared with E_A. The angle ϕ, between grains, is also weakly dependent upon time of operation. In practice the product of these parameters may be assumed to be constant that is the parameter *a* is treated as constant [11]. However, the effect of variation of other parameters, namely, the grain growth exponent, activation energy and hot side temperature on the grain size of electrode materials, as time of operation goes by, is worth studying. This in turn will determine the thermo-electro-chemical behavior of electrodes and thus the power output. The grain growth exponent, activation energy and hot side temperature are inherent parameter of the characteristic of electrode materials, but time of operation is dictated by the time needed of using AMTEC.

5. RELATION BETWEEN GRAIN SIZE AND POWER OUTPUT

The experimental studies of grain growth rates for various materials have been performed and established an empirical correlation between grain size of electrode materials and the power output [10, 13]. An algorithmic simulation study by Lodhi and Chowdhury was performed to investigate the power output of practical use within the realistic range of grain size [14]. Using the approach taken by these two above mentioned studies a recent paper has provided a direct algorithm relationship of the power output of AMTEC and the grain size of electrode material, characterized by parameters *a*, E_A and *n,* depending on time and temperature given by [15]:

$$P_e = 1.5135 + 0.006 * (B_o - bR_f^{1/2}) - (B_o - bR_f^{1/2})^2 * 1\times10^{-5}, \qquad (3)$$

where B_o is a constant and assumed to be 270 $AK^{1/2}m^{-2}pa^{-1}$ and *b* is the coefficient of pertaining to the grain size of the material used and has been determined experimentally as 6.218 [10].

As a test case we study the grain size variation of Molybdenum (Mo) as the inherent parameters are allowed to vary within reasonable ranges for the operation of AMTEC from two to sixteen years invoking equation (1). The long period of time is included for the potential use of AMTEC in deep space missions. The corresponding values of grain sizes may be used in equation (3) for calculating the power output and its degradation over the required period of time.

6. SIMULATION RESULTS

Figures 2–4 show the effect of variation of *n,* E_A and *T* on grain size for segments of time ranging from 20,000 hours to 140,000 hours with interval of 20,000 hours. The grain size varies sharply for changes in smaller values of n. It is almost insensitive to changes in n when it assumes a

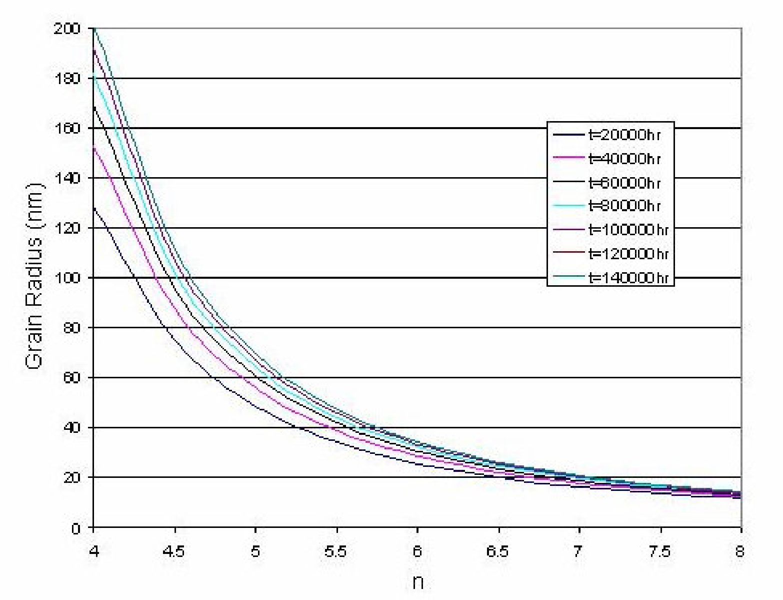

Figure 2. The Variation of Grain Radius with n for Mo

large value around 7, see figure 2. In figure 3 the grain size is simulated to vary, around the known value of E_A for Mo, 814.06 kJ/mole, ranging from 700 kJ/mole to 950 kJ/mole in increments of 50 kJ/mole. The grain size varies sharply for changes in E_A for smaller values. It is almost insensitive to changes in E_A for high values. In figure 4 the grain size varies over a range of temperature from 1050 K to 1250 K, The reason for this temperature span used in this simulation is because the experimental observations indicate that the parameter a remains constant in this range of temperature for Mo [11].

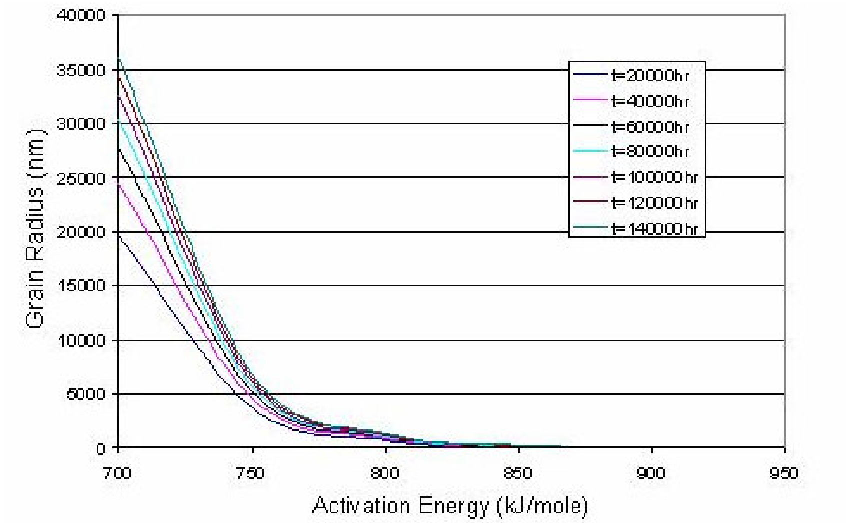

Figure 3. The Variation of Grain Radius with Activation Energy for Mo

large value around 7, see figure 2. In figure 3 the grain size is simulated to vary, around the known value of E_A for Mo, 814.06 kJ/mole, ranging from 700 kJ/mole to 950 kJ/mole in increments of 50 kJ/mole. The grain size varies sharply for changes in E_A for smaller values. It is almost insensitive to changes in E_A for high values. In figure 4 the grain size varies over a range of temperature from 1050

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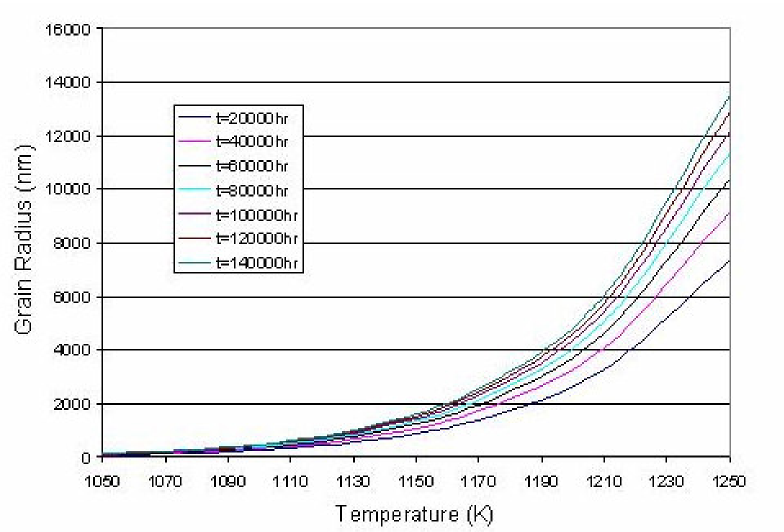

Figure 4. The Variation of Grain Radius with Temperature for Mo

The power output at the very outset (time = 0) can be calculated by replacing R_f with Ro = 10 nm. It may, however, be calculated after any laps of time by invoking equations (1) and (3). The power degradation percentage over a period of 140,000 hours is presented in Table 1. for a set of three parameters.

Table 1. Percentage power degradation over 140,000 hours

n	E_A	T	P_e %
6.5	814	1150	3
3.2	950	1150	7
4.0	814	1050	15

7. CONCLUDING REMARKS

The power output of the AMTEC cell is greatly affected by the choice of electrode materials with respect to grain size growth. To use AMTEC for a long period of time, we have investigated for thermo-chemical conditions Mo electrodes, which least affect the degradation of power output, when used for about 15 years. These conditions can be generalized for other electrode materials, and that is the way we interpret the results obtained in this study. The power degradation is strongly coupled with the growth of the grain size of the electrode materials. We found that grain growth is sensitive to the parameters, initial grain size, growth exponent *n*, activation energy E_A, temperature of the hot side of the AMTEC cell *T* and the time of operation *t.* This study has focused on improving the thermo-chemical performance of the electrode by adjusting certain conditions that are inherent to the electrode materials with respect to time. These conditions are grain growth parameters involved in the grain mobility model for grain growth of electrode materials. If the grain size of the electrode material reaches a certain dimension, about 500 nm, it no longer functions efficiently. This is very important because this condition should not occur until after the time desired for operation has elapsed.

The effect of altering *n*, the growth exponent, in the grain growth equation on the behavior of the grain size for any material, in principle, is universal. The experimental value of *n* has been determined between 3 and 6.5 depending upon the material. If the grain growth of the material is regulated more by volume diffusion than surface diffusion at the grain boundary, it will be closer to 3. If the grain growth of the material is regulated more by surface diffusion than volume diffusion at the grain boundary, it will be closer to 4. This demonstrates that as *n* increases, R_f decreases. Since power degradation is dependent upon increasing of the grain size, the choice of material with higher *n* should lessen the grain growth over the operation time and keeps the power degradation low.

The effect of varying activation energy in the grain growth equation on the behavior of the grain size of the material is also like that of *n*. The activation energy is the amount of energy that is needed to allow the grain boundaries to begin expanding within the material. Conceptually this tells us that higher the activation energy a material has, slower the grain will grow over the time due to a larger energy barrier to grain boundary expansion.

The effect of altering the temperature *T*, of the electrode on the hot side, in the grain growth equation on the behavior of the grain size of the material is reverse as those of .*n* and $E_{a.}$ This specific *T* corresponds to the hot side of the AMTEC device where the electrode is exposed to high temperature and pressure. This demonstrates that as T increases, R_f increases. Obviously for longer life of electrodes AMTEC should be operated at the minimum optimum temperature. This study urgently recommends to experimentally determine the inherent parameters *n,* E_f and *T* of materials of interest for electrodes in sodium (alkaline) environment. Alternatively, one maylook or prepare alloys and/or ceramics with high activation energy, operating at low temperature with appropriate growth exponent parameter *n.*

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References

1. Ryan et al., “Performance Parameters of TiN Electrodes for AMTEC Cells, “Space Technology and Applications International Forum, 1301 (1999) 1303
2. Hunt, T.K., N. Weber, and T. Cole, “Research on the Sodium Heat Engine,” Proceedings of the 13th Intersociety Energy Conversion Engineering Conference, SAE, Warrendale, PA, 2011, (1978)

3. R. Mital et al., “Performance Evaluation of Gas Fired AMTEC Power Systems,” Advance Modular Power Systems, Inc., USA, 1-2, (1998).
4. M.A. Ryan et al., *J. Electrochem. Soc*., 142 (1995) 4252
5. Sievers, R.K., and C.P. Bankston, “Radioisotope Powered Alkali Metal Thermoelectric Converter Design for Space Systems,” 23rd IECEC, 3, (1988).
6. R.M. Williams et al., “Kinetics and Transport at AMTEC Electrodes–I. The Interfacial Impedance Model,” *J. Electrochem. Soc.,* 137 (1990) 1709
7. Cole, T., *Science*, 221 (1983) 915
8. Brad Fiebig, Michael Schuller, Margaret Amy Ryan, Roger Williams, and Patricia Hudson, “Advanced Electrodes for AMTEC”, Space Technology and Applications International Forum-1999, *American Institute of Physics,* 1999.
9. Margaret A. Ryan, Roger M. Williams, Mark L. Underwood, Barbara Jeffries-Nakamura and Dennis O'Connor, "Electrode, Current Collector and Electrolyte Studies for AMTEC Cells," *American Institute of Physics Conference Proceedings* 1993, Issue 271/2, pp. 905-912. Pub: American Institute of Physics; 1993
10. T. K Hunt et al., “Solid State Electrode Systems for the Sodium Heat Engine,” Proc. Second Symp. on Electrode Mat. And Processes for Energy Conversion and Storage, Electrochemical Society, 608 (1987) 87.
11. M. A. Ryan et al., “Lifetimes of AMTEC Electrodes: Molybdenum, Rhodium-tungsten, and Titanium Nitride,” Space Technology and Applications International Forum-2000, Edited by El-Genk, M.S., 2 (2000) 1377
12. V. B. Shields et al., “Model for Grain in AMTEC Electrodes,” Intersociety Energy Conversion Engineering Conference, N.Y., 1-3, (1999).
13. M.A. Ryan, A. Kisor, R.M. Williams, B. Jeffries-Nakamura, and D. O’Connor, “Lifetimes of thin film AMTEC electrodes, ”Proc. 29th IECEC, 2 (1994) 877
14. Lodhi, M.A.K., M.S. Chowdhury, *J. Power Sources* 103 (2001) 18
15. M. A. K. Lodhi and J. B. Briggs, “Temperature Effect on Lifetimes of AMTEC Electrodes,” *J. Power Sources*, to be published