

Temperature-dependent grain growth model for AMTEC electrodes

M.A.K. Lodhi^{a,b,*}, Siew Choo Soon^c, M. Mohibullah^c

^a ITMA, Department of Physics, University Putra Malaysia, Malaysia

^b Department of Physics, Texas Tech University, Lubbock, TX 79409, USA

^c Department of Electrical Engineering, University Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

Received 5 March 2004; accepted 22 March 2004

Available online 15 June 2004

Abstract

Electrode materials for AMTEC play a significant role in its power output and efficiency. TiN, RhW and Rh₂W alloys have been studied to determine the best performing material over a wide range of temperature ~1000–2000 K. The power output is related to the grain growth of the electrode material. By simulation and analysis this study examines power degradation of AMTEC due to the grain size and leads to the performance of RhW material as best among them.

© 2004 Published by Elsevier B.V.

Keywords: AMTEC; Electrodes; Grain size; Power degradation; Temperature dependency

1. Introduction

The direct energy conversion static devices are receiving increasing attention particularly for their use in space. Alkali metal thermal to electric converter (AMTEC) has been a strong candidate as a static thermal to direct electric converter for space as well as terrestrial uses. This device has a promise for high efficiency, close to Carnot efficiency, power density and long life with minimal power degradation. These are most desirable qualities for space mission power generation and management. The ground uses of AMTEC are currently in performance analyses of gas cooled reactors and liquid metal cooled reactors small power plants. For such a promising future of AMTEC agencies like DARPA, US Air force, DoE, and NASA, besides NSF are very supportive of this technology. These features have been discussed extensively in a short communication and references therein [1].

Much of the development of AMTEC has been done relating to space power. During an extended testing of AMTEC in the Air Force Research Laboratory, the maximum output power was observed to be decreasing from 2.48 to 1.27 W after 18,000 h of actual operation. The temperatures of the hot and the condenser sides were maintained, respectively, 1023 and 600 K throughout the operation [2]. Recent studies show that the electrolyte and the electrodes used in AMTEC

PX-3A are two of the most degrading components [3–11]. In this work we examine theoretically by simulating PX3 model of AMTEC by the computer and analyze its life acceleration performance equivalent to 15 years over a large range of temperature. The temperature range is varied only at its hot end. The condenser side is kept at a fixed temperature of 623 K.

The PX-3A AMTEC is divided in two regions by its electrolyte which is beta alumina solid electrolyte (BASE). A high pressure, high temperature region within its range 10–100 kPa and 900–1300 K, respectively, is confined within a cylindrical BASE. The other region is located outside the cylindrical BASE designated as low pressure, low temperature region within the range <50 Pa and 400–700 K, respectively. A porous metal covering the low pressure (outer) side acts as a cathode. A similar metal covering the inner surface of the BASE at high pressure, high temperature region performs the role of an anode (see Fig. 1). In this work different materials for electrodes are used and analyzed. Both electrodes provide a conduction path for electrons to and from the external load. Sodium is used as a working fluid and the BASE as the ionic conductor. Sodium enters the hot region of the cell in the vapor form. Due to the thermodynamical potential across the BASE, ionization of sodium occurs in the hot region at the interface of BASE and anode:



The sodium ions are diffused through the BASE to the cathode due to the pressure differential across the BASE. The

* Corresponding author. Tel.: +1-806-742-3778; fax: +1-806-742-1182.
E-mail address: a.lodhi@ttu.edu (M.A.K. Lodhi).

Nomenclature

b	electrode exchange current constant
B	temperature-independent exchange current ($\text{A K}^{1/2}/\text{Pa m}^{1/2}$)
B_0	initial temperature-independent exchange current ($\text{A K}^{1/2}/\text{Pa m}^{1/2}$)
c	proportionality constant
E_A	activation energy for grains to move to the grain boundary
M_0	mobility constant
n	constant, characteristic of the electrode material
P_e	electrical power output
R_a	average grain radius
R_0	average initial grain radius
t	time
T	electrode temperature (K)

Greek letters

γ_s	individual surface energy of the grain boundary
ϕ	angle by which two grains are separated

electrons are collected at the electrode, circulate through the external load producing electrical work and then reach the cathode surface, where they recombine with the sodium ions at the interface of the BASE and cathode:



The neutralized sodium vapor leaves the porous cathode, moves through the low pressure region of the cell and releases its heat condensation on the condenser surface. Nearly entire temperature drop occurs in this low pressure vapor space. The condensed liquid sodium moves to a wick annulus to the inlet of a small electromagnetic pump or a porous capillary wick, which is used to bring the sodium to an evaporator in the high pressure region. At the evaporator the liquid sodium is converted to the vapor form to enter the BASE. In this way the closed cycle of sodium is completed. The heat is supplied from an external source to the cell by means of a hot plate. The hot plate, in turn, transfers heat to the evaporator and the BASE tubes by radiation and conduction through the thermal rings.

2. Role of the electrode materials

AMTEC cell with TiN electrodes have relatively large internal electrical losses [12]. These electrodes are about 90% porous. Their temperature exchange current, B is relatively low, and the contact resistance between the BASE, electrode and current collector is relatively large. Accordingly, the concentration losses in the cell (the effect of sodium vapor pressure at the BASE/cathode interface) are small,

compared to the charge–exchange polarization and internal ohmic losses. The replacement of electrode materials, with lower interfacial contact resistance and higher temperature exchange current would improve the cell's performance. The time-dependant impact of the electrodes on power degradation of AMTEC cell is important. In recent papers [6,7], the steady-state analysis shows that porosity, resistivity, conductivity and nature of contact between the electrodes and electrolyte are time limiting phenomena. All of these factors stem from the surface self-diffusion and grain growth effect of electrode materials. The sintering of the electrode materials at high temperature (500–1200 K) affect those factors adversely. As the grains sinter, they increase in size and coalesce, thus increasing the void (porosity) in the electrode materials. This leads to less contact between the electrode and electrolyte, thus causing the higher resistivity. It was concluded that grain growth is responsible for degradation of all time-dependant factors mentioned above.

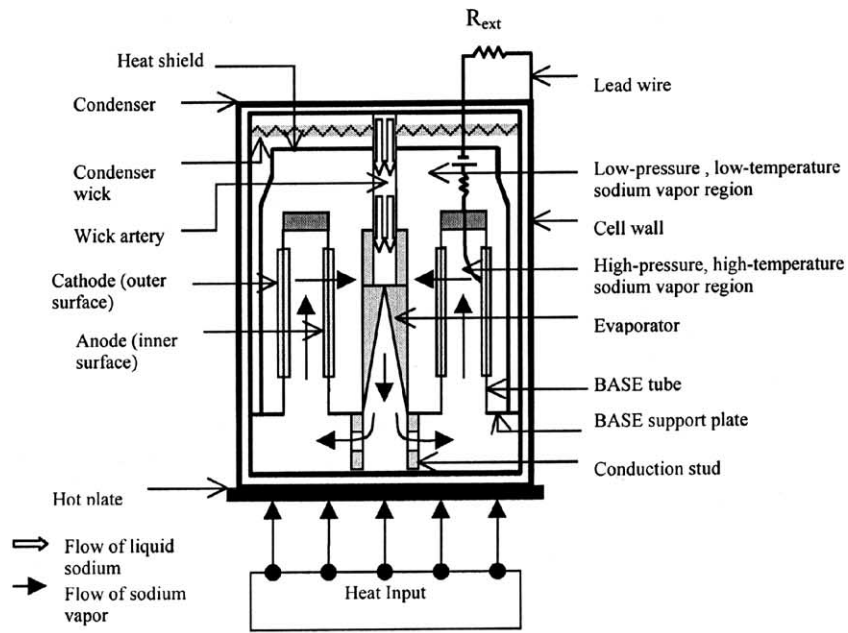
In recent work, three materials TiN, RhW and Rh₂W were simulated over a period of 15 years to test the performance of AMTEC at a fixed temperature of 1023 K at the hot side and 600 K at the condenser side. From the grain growth effect the performance of RhW electrode was found best [7]. Since the sintering effect is sensitive to the temperature change; it seems appropriate to study the time-dependent characteristics of those materials with respect to the power degradation of AMTEC. In this work the time-dependent characteristics of the electrode materials, TiN, RhW and Rh₂W are studied over a large range of temperature, for a simulated mean life period of accelerated operation, equivalent to 15 years.

3. Time, temperature and grain size relation

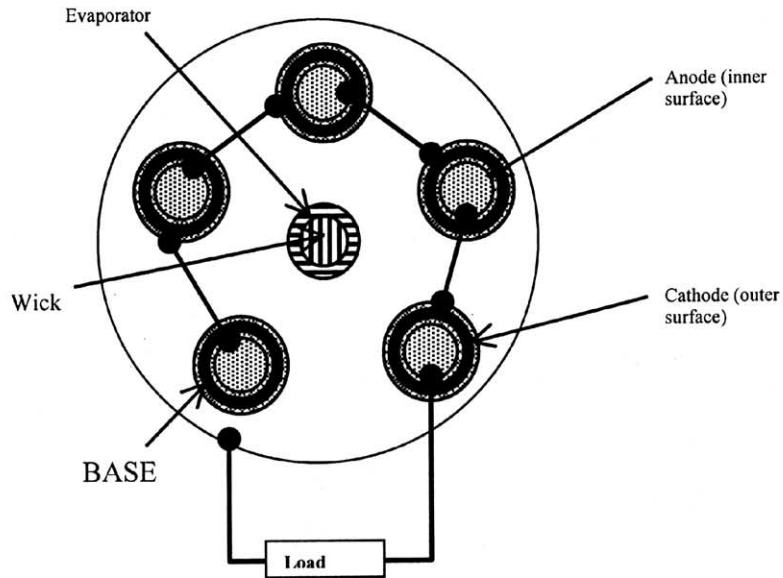
The transient behavior of grain size growth is important in determining the electrode degradation and hence the overall power degradation of the cell. Once the relation between grain size, time and temperature is found, the grain size is next to be related with same parameters(s) of electrode that determine its performance. The approach we take is to correlate the grain size with the temperature exchange current, which, in fact, is a measure of contact between the electrodes and the electrolyte [11]. The power output is almost directly dependent on the exchange current [6,7]. A model for grain growth as a function of time and temperature is given by [9]:

$$R_a = R_0 \left[1 + 2cM_0R_0^{-n}\gamma_s \cos \phi t \exp\left(\frac{-E_A}{RT}\right)^{1/n} \right] \quad (3)$$

where R_a is the average grain radius at any time t at any temperature T , R_0 the average initial grain radius, c a proportionality constant that provides for correct dimensionality, M_0 the mobility constant, γ_s the average individual surface grain boundary energy, ϕ the angle arising from a balance of force due to surface tension and the pressure at the grain



(a)



(b)

Fig. 1. PX-3A AMTEC: (a) front view and (b) top sectional view.

boundary, or an angle separating the two adjacent grains, E_A the activation energy for grains to move to the grain boundary and the parameter n is estimated to be 3.2. An empirical relation between grain size and temperature independent exchange current B is found to be [11]

$$B = B_0 - bR_a^{12} \tag{4}$$

where B_0 is the initial temperature independent exchange current and b the electrode exchange current constant to be

determined experimentally for various materials. The relation between power output P_e and B has been obtained from the simulation technique in previous work [6,7] as

$$P_e = 1.5135 + 0.006B - 10^{-0.5B^2} \tag{5}$$

These three equations (3)–(5) provide the temperature-dependent performance of the materials for electrodes over long period of time, a simulated life-time operation equivalent to 15 years. This study will complement the

Table 1
Relevant parameters for electrode material

Material	E_A (kJ/mol)	B_0 (A K ^{1/2} /Pa m ^{1/2})	b (A K ^{1/2} /Pa m ^{2.5})	R_0 (nm)	a (10 ¹²)	c	M_0 (m/s)	γ_s (J/m ²)
TiN	175.50	270	6.218	30	1.14	270		
RhW	260.51	270	5.4222	30	4.34		2.25×10^{-5}	2.839
Rh ₂ W	206.48	270	5.4222	30	4.34		1.3×10^{-1}	2.745

Table 2
Power output and efficiency for life acceleration equivalent to 15 years of operation of AMTEC with cold side temperature = 623 K

	Hot side temperature (K)					
	1225	1300	1400	1500	1600	1700
TiN ($B = 150.80$)						
Power output (W)	5.51	7.14	9.49	11.94	14.32	16.22
Efficiency (%)	14.13	15.61	17.22	18.45	19.33	19.85
Rh₂W ($B = 197.48$)						
Power output (W)	5.65	7.29	9.64	12.09	14.46	16.36
Efficiency (%)	14.39	15.48	17.41	18.61	19.46	19.97
RhW ($B = 238.27$)						
Power output (W)	5.74	7.37	9.72	12.17	14.54	16.44
Efficiency (%)	14.54	15.97	17.51	18.69	19.54	20.04

previous study, which was a time-dependent performance of electrode material at fixed temperatures at the hot and condenser ends. In this work the temperature at the condenser end is kept the same throughout whereas the hot end temperature is varied until a peak for the power output is reached.

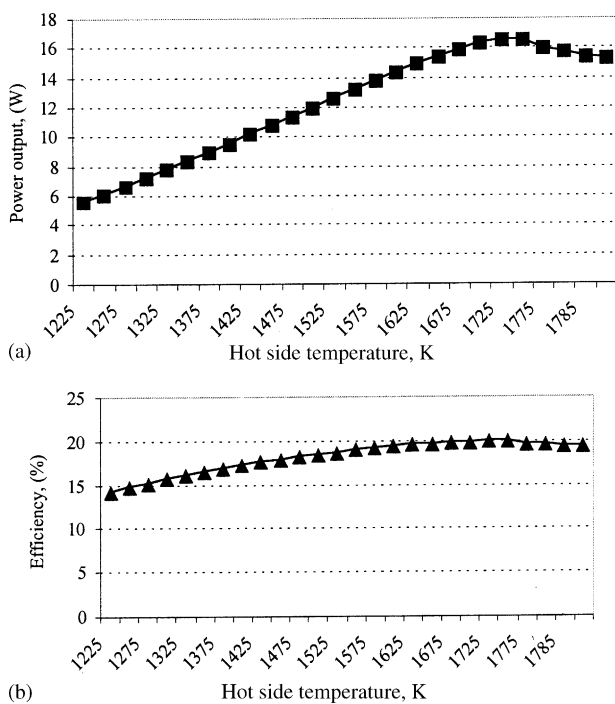


Fig. 2. Simulated power output (a) and efficiency (b) with TiN electrodes after 15 years operation.

A parameter a , defined as

$$a = 2cM_0\gamma_s \cos \phi \tag{6}$$

to be inserted in Eq. (3), has been evaluated for the three different electrode materials under investigation. Its values are given in Table 1, calculated from the values of the parameters also given in it. The values used for other parameters like, gas constant R is 8.314 J/mol, n is 3.2, $\phi = 30^\circ$ for small grain size [9] and $t = 129,600$ h.

The power output, P_{out} , according to Eq. (5) depends nonlinearly on the temperature-independent exchange current, B , which in turn depends on the grain size R_a . We are not presenting the variation in the values of R_a and B as a function of time. This was done over a large range of time, 140,000 h, recently for these three electrodes [7]. For TiN the grain size matches reasonably well, for small grains, with the model projection results and observed values up to 100,000 and 1800 h, respectively, reported by Shields et al. [9]. As to the results of RhW and Rh₂W there is nothing available to compare with. In this work we are concentrating at the power output and the efficiency at a large range of temperature, 1000–2000 K.

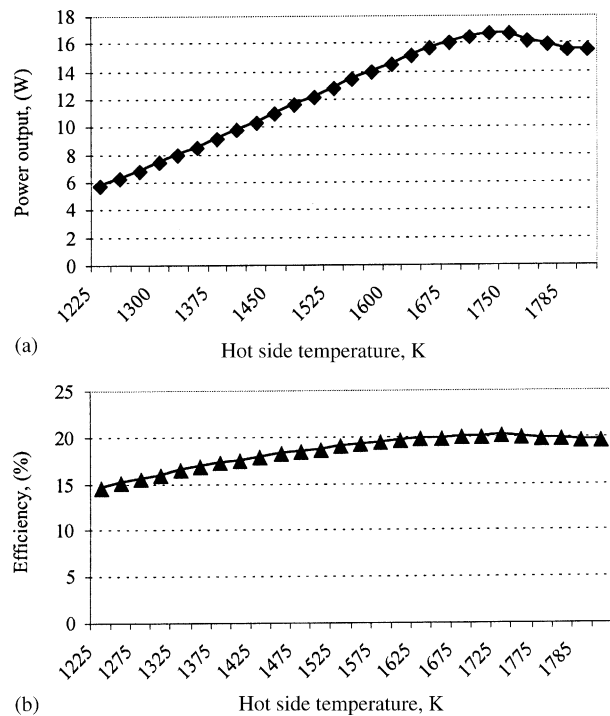


Fig. 3. Simulated power output (a) and efficiency (b) with RhW electrodes after 15 years operation.

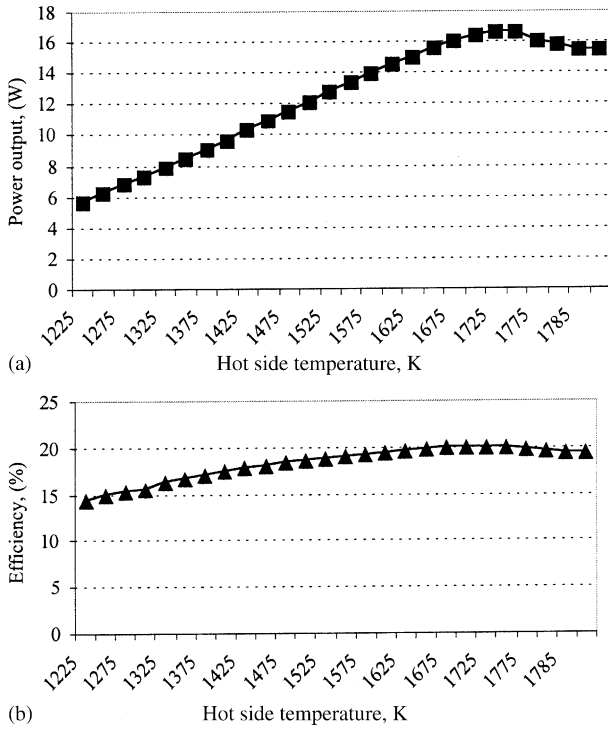


Fig. 4. Simulated power output (a) and efficiency (b) with Rh₂W electrodes after 15 years operation.

4. Results

We simulated the power output and efficiency of AMTEC for a range of temperature from 1000 to 2000 K in three different cases given in Table 2 and Figs. 2–4 for life acceleration operation equivalent to 15 years. (These figures and all subsequent figures are meant to be for life acceleration operation equivalent to 15 years but for brevity sake the phrase after 15 years operation is used.) These results are for AMTEC electrodes materials, TiN, RhW and Rh₂W. The power output peak is observed around 1750 K regardless of the electrode materials used. As we calculate the degradation of the power output and that of the efficiency for those materials. There is a distinct difference among them as evidenced by Table 3 and Figs. 5–7. A comparative presentation of degradation of power output and efficiency for those materials is given in Figs. 8 and 9.

To calculate these results an 18,000-line FORTRAN code has been used to simulate and analyze the transient behavior of AMTEC. This code is based on four principle models: (1) vapor pressure loss model, (2) electrochemical model, (3) thermal model, and (4) electrical model [12]. The grain growth effect is introduced [6,7] to this FORTRAN model following the approach taken by Shields et al. [9].

Table 3

Temperature-dependent degradation performance of AMTEC for life acceleration equivalent to 15 years of operation with cold side temperature = 623 K

	Hot side temperature (K)							
	1000	1100	1200	1300	1400	1500	1600	1700
TiN (B = 150.80)								
Initial power output (W)	1.92	3.41	5.27	7.42	9.77	12.21	14.58	16.48
Initial efficiency (%)	8.94	11.74	14.10	16.04	17.57	18.74	19.58	20.08
Final power output (W)	1.70	3.16	5.00	7.14	9.49	11.94	14.32	16.22
Final efficiency (%)	8.18	11.10	13.58	15.61	17.22	18.45	19.33	19.85
Power output degradation (W)	0.00	0.25	0.27	0.28	0.28	0.27	0.26	0.26
Power output degradation (%)	11.46	7.33	5.12	3.77	2.87	2.21	1.78	1.58
Efficiency degradation (%)	0.76	0.64	0.52	0.43	0.35	0.29	0.25	0.23
Rh₂W (B = 197.48)								
Initial power output (W)	1.92	3.41	5.27	7.42	9.77	12.21	14.58	16.48
Initial efficiency (%)	8.94	11.74	14.10	16.04	17.57	18.74	19.58	20.08
Final power output (W)	1.81	3.29	5.14	7.29	9.64	12.09	14.46	16.36
Final efficiency (%)	8.57	11.43	13.85	15.84	17.41	18.61	19.46	19.97
Power output degradation (W)	0.11	0.12	0.13	0.13	0.13	0.12	0.12	0.12
Power output degradation (%)	5.73	3.52	2.47	1.75	1.33	0.98	0.82	0.73
Efficiency degradation (%)	0.37	0.31	0.25	0.20	0.16	0.13	0.12	0.11
RhW (B = 238.27)								
Initial power output (W)	1.92	3.41	5.27	7.42	9.77	12.21	14.58	16.48
Initial efficiency (%)	8.94	11.74	14.10	16.04	17.57	18.74	19.58	20.08
Final power output (W)	1.88	3.37	5.22	7.37	9.72	12.17	14.54	16.44
Final efficiency (%)	8.81	11.63	14.01	15.97	17.51	18.69	19.54	20.04
Power output degradation (W)	0.04	0.04	0.05	0.05	0.05	0.04	0.04	0.04
Power output degradation (%)	2.08	1.17	0.95	0.67	0.51	0.33	0.27	0.24
Efficiency degradation (%)	0.13	0.11	0.09	0.07	0.06	0.05	0.04	0.04

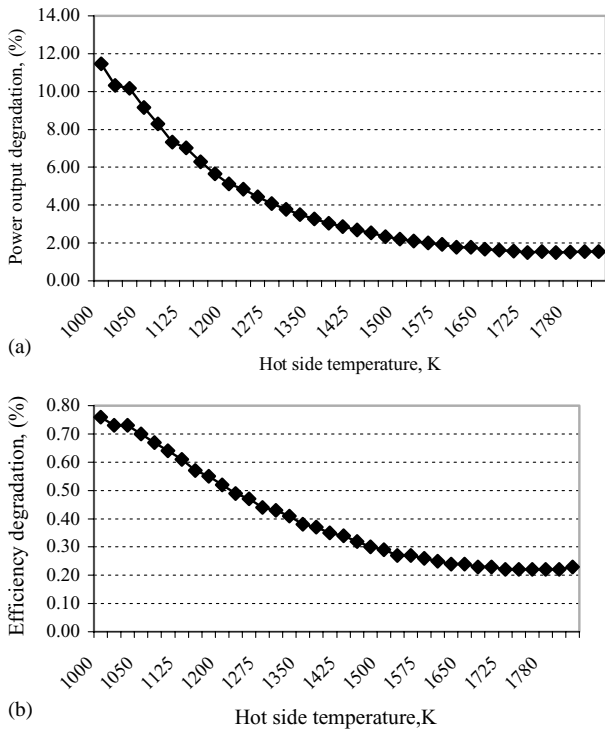


Fig. 5. Simulated power output degradation (a) and efficiency degradation (b) with TiN electrodes after 15 years operation.

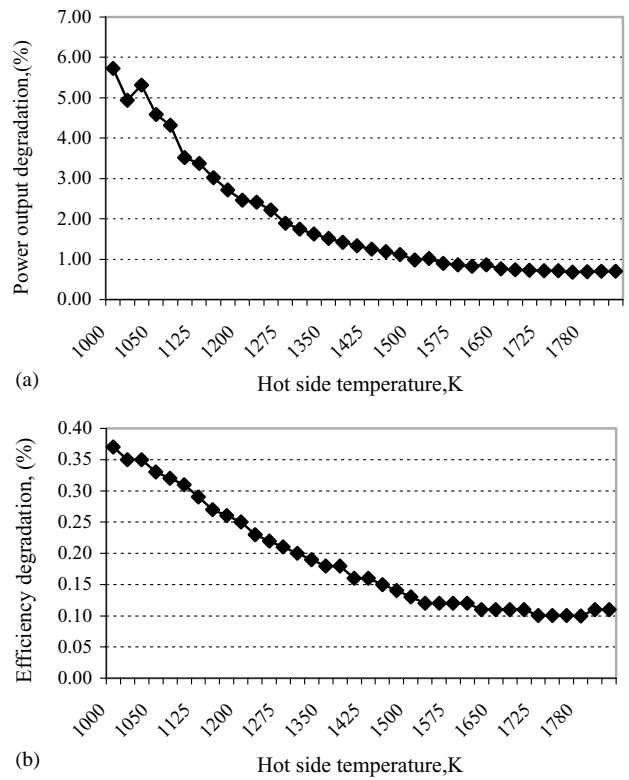


Fig. 7. Simulated power output degradation (a) and efficiency degradation (b) with Rh₂W electrodes after 15 years operation.

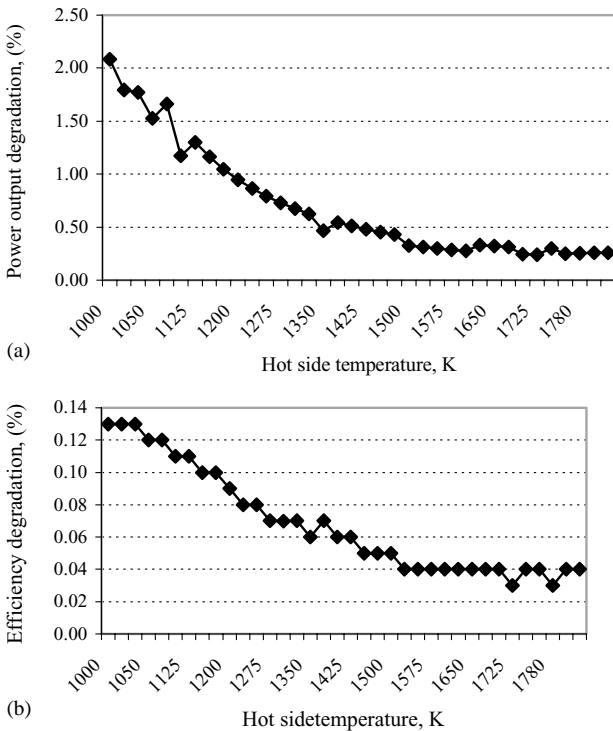


Fig. 6. Simulated power output degradation (a) and efficiency degradation (b) with RhW electrodes after 15 years operation.

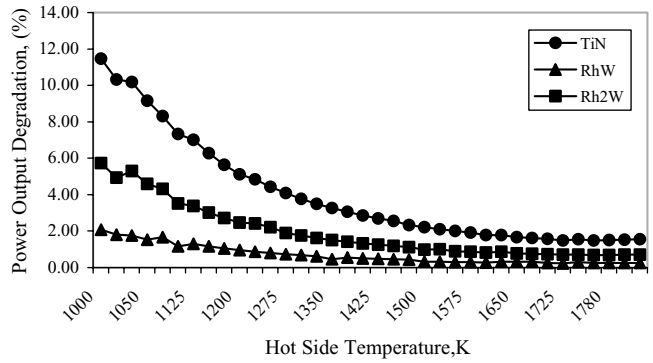


Fig. 8. Comparison of simulated power output degradation after 15 years operation with TiN, RhW and Rh₂W electrodes.

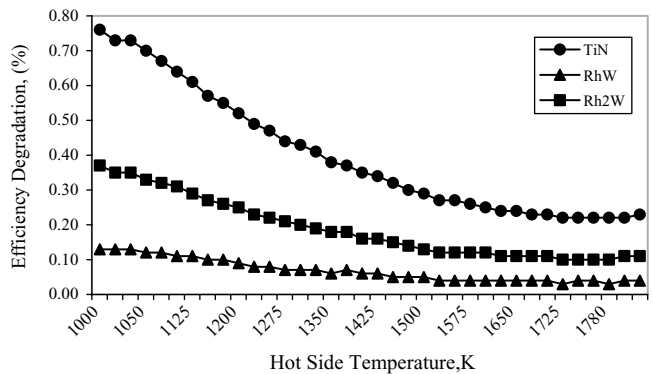


Fig. 9. Comparison of simulated efficiency degradation after 15 years operation with TiN, RhW and Rh₂W electrodes.

5. Conclusion

The present model for AMTEC electrode displays a definite preference for RhW over Rh₂W and TiN materials. This model is based on the grain growth of the materials under investigation. The simulation for TiN grain growth is comparable to the model used by Shields et al. [9] and to the measured data for a small range of temperature. However, the results for extended growth rate of grains need to be supported by longer term observed data over a wide range of temperature for these materials, namely, TiN, RhW and Rh₂W.

From Figs. 8 and 9 the power degradation and efficiency degradation is least for RhW compared to Rh₂W and TiN throughout this range of temperature. It must be borne in mind that the AMTEC performance of power output and efficiency has been studied on the basis of the grain size effect of its electrode materials. The grain size is influenced by time and temperature both. In this simulation the time is kept the same for calculating its performance (power output) at various temperature. In practice, however, it is the time which is varied whereas the temperature is kept the same. This study provides the optimum temperature for the power output and the efficiency. In an earlier study the simulation was performed for the same set of electrodes at a fixed temperature of 1023 K over a simulated period equivalent to 15 years [7]. It may be interesting to see the corresponding performance of AMTEC at some temperatures significantly different than 1023 K.

This study is done on the grain growth model [9] in which the small size grain is taken into consideration at the lower limit. The results of course, agree with the observed data for a short period (1800 h) [9]. A similar simulation is recommended at the upper limit of the grain size of the model. Alternatively, based on a different model, designed by other approach, theoretical or empirical studies may be performed to obtain the best results. This model may have a wider scope than just including the grain size, depending on time and temperature. There may be other effects causing the degradation such as, chemical reaction between the electrolyte and electrodes. Besides the electrode there are other components in the AMTEC which could be the cause for degradation of power. Among those are included BASE, cell wall, artery, evaporator, heat shield, etc. We know that

BASE is the main cause of power degradation. It may alone contribute to the degradation as much as 50–60% [4]. The power degradation due to electrode is estimated as 15–19% [6]. Conclusively evident is from this study that the properties of electrode materials change with time and temperature due to the grain size causing the degradation of the AMTEC performance. Nevertheless, RhW is by far the least affected among the materials examined due to the temperature variation.

References

- [1] M.A.K. Lodhi, P. Vijayaraghavan, A. Daloglu, An overview of advanced space/terrestrial power generation device: AMTEC, *J. Power Sour.* 103 (2001) 25.
- [2] M. John, AFRL, Albuquerque, NM, Personal Communication.
- [3] M.A.K. Lodhi, P. Vijayaraghavan, A. Daloglu, Time-dependent BASE performance and power degradation in AMTEC, *J. Power Sour.* 93 (2001) 41, and references therein.
- [4] M.A.K. Lodhi, P. Vijayaraghavan, A. Daloglu, Simulation and analysis of time-dependent degradation behavior of AMTEC, *J. Power Sour.* 96 (2001) 243.
- [5] M.A.K. Lodhi, A. Daloglu, Effect of radiation shield on pressure losses and power output of AMTEC cell, *J. Power Sour.* 93 (2001) 258.
- [6] M.A.K. Lodhi, M.S. Choudhury, The role of electrodes in power degradation of AMTEC: analysis and simulation, *J. Power Sour.* 96 (2001) 769.
- [7] M.A.K. Lodhi, M.S. Choudhury, Characteristics of electrodes materials and their lifetime modeling for AMTEC, *J. Power Sour.* 103 (2001) 18.
- [8] M.A. Ryan, et al., Advances in materials and current collecting networks for AMTEC electrodes, *J.P.L. Cal. Tech.* (1992) 37–311.
- [9] V.B. Shields, et al., Model for grain in AMTEC electrodes, in: *Proceedings of the Intersociety Energy Conversion Engineering Conference*, New York, 1999, pp. 1–3.
- [10] R.M. Williams, et al., Kinetics and transport at AMTEC electrodes, Part II, Temperature dependence of the interfacial impedance of Na(g)/porous Mo/Na-beta alumina, *J. Electrochem. Soc. (Honolulu)* 137 (1990) 716.
- [11] M.A. Ryan, et al., Lifetime of AMTEC electrodes: molybdenum, rhodium–tungsten and titanium nitrate, in: M.S. El-Genk (Ed.), *Space Technology and Applications, International Forum-2000*, vol. 2, 2000, pp. 1377–1382.
- [12] J.M. Tournier, M.S. El-Genk, M. Schuller, P. Hourger, An analytical model for liquid-anode and vapor-anode AMTEC converters, in: M.S. El-Genk (Ed.), *Proceedings of the Space Technology and Applications International Forum, CONF-970115*, vol. 3, No. 387, AIP, New York, 1997, pp. 1543–1552.