



Kinetic Study on Anodic Growth of Film on Tantalum in Aqueous Succinic Acid

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Abstract

The present manuscript attempts to investigate the anodic growth of film on tantalum at various current densities (2.5, 5.0, 10.0 and 15.0 mAcm⁻²) in presence of 0.1N solutions of succinic acid (prepared in 1:1 v/v of ethanol + water) at four different temperatures (288.15, 298.15, 308.15 and 318.15K). The constants A and B of Guntherschulze-Betz empirical equation have been determined. The value of A varied with temperature but the value of B was found independent of temperature, which implies the non-dependence of Tafel slope on temperature. Quadratic variation of field strength with ionic current density was examined critically in view of Dignam model. The zero field activation energy (ϕ), dimensionless quantity (C), zero field activation dipole (μ^*), net activation energy W (E) and Morse function parameter (w^*) of Dignam model were evaluated. The effects of temperature and current density on various parameters of Dignam model have been discussed. Quadratic term contributed significantly which elucidates that single-barrier theory does not explain the data satisfactorily.

Keywords: Anodic oxidation, Tantalum, Tafel slope, Dignam model, Guntherschulze-Betz equation.

Introduction

Considerable efforts have been made in the past to investigate the properties and mechanism of the growth of anodic oxide films on valve metals. On anodization, metal can undergo a variety of oxidation reactions e.g. anodic-oxide growth, oxygen evolution, anodic dissolution and oxidation of solute components of the electrolyte. The growth of anodic oxide film is essentially a problem in ionic conduction at high field strength complicated by the presence of two interfaces, i.e. metal/oxide and oxide/solution at which transfer process must occur. Anodic oxide films can be formed on valve metals by any of the three methods i.e. galvanostatically, potentiostatically and by a sequence of constant current and constant voltage.

Anodic oxidation of valve metal plate in an aqueous acidic solution is a widely accepted technique for preparing oxide films with high bonding strength and has become an important process for improving the surface chemistry of metal in areas such as corrosion science and semi-conductor technology¹. The high dielectric constant and high breakdown potential make these anodic oxide films particularly useful in the industrial chemical processes related to electronic devices, batteries, thin film transistors, corrosion protection films, fuel cells, thin film devices, nuclear technology, rectifiers and in capacitor technology as dielectric, marine engineering and insulating materials²⁻⁶. Ta₂O₅ thin films offer a six-fold increase in dielectric constant compared to conventional dielectrics, so they can be used in the fabrication of a reliable high-density memory devices. These thin films are useful in themselves as protective

and decorative coatings over the metal substrate.

The kinetics of the growth of films on valve metals for a long time has been interpreted in terms of high field ionic conduction equation i.e. $i = A \exp(BE)$, where i is current density, E is the electric field strength in the film, A and B are positive temperature dependent constants. This relation is also known as Guntherschulze-Betz equation⁷. Various other models have been proposed to explain the growth kinetics but divergent views have been expressed by the different workers⁸⁻²⁴. According to Cabrera and Mott, the Tafel slope should be proportional to temperature⁸. However, Young found that the Tafel slope is independent of temperature¹³. Young and Dignam took into account the quadratic variation of field with ionic current density to explain the field and temperature dependence of Tafel slope^{11, 13}. It appears that the exact behavior of Tafel slope with temperature needs a thorough probing. The perusal of literature reveals that the results obtained by different workers are at variance.

In the present study, steady state kinetics for anodic growth of film on tantalum in 0.1N succinic acid at a wide range of temperatures and current densities has been investigated. The behavior of Tafel slope and various parameters of Dignam model have been evaluated.

Material and Methods

The anodic growth of oxide film on valve metal is very sensitive to the method of surface preparation of sample and hence to

obtain reproducible results, many precautions are necessary to be taken during the preparation of specimen's surface. The following procedure was used in the present study.

Technique for the preparation of surface of specimen for anodic polarization: Square tantalum samples (Area = 2cm²) with a short tag were cut by a die from a tantalum sheet of 99.9% purity (Aldrich chemical company, U.S.A.). The edges of the specimen were abraded with 600 grit emery paper to make the surface smooth. The specimens were cleaned with acetone to remove the greasy particles, dipped in KOH melt to clean the surface and washed with doubly distilled water. The chemical polishing was done by dipping sample in freshly prepared etching mixture of 98% H₂SO₄, 70% HNO₃ and 48% HF (5:2:2 v/v) for 3-5 s and then washed with distilled water. The specimens were placed in boiling water for 10 minutes so as to remove any impurity left sticking to the surface. Finally, the sample was dried in a current of hot air. The entire process was repeated just before the use of the sample. The above process removed all the scratches and foreign materials and left a smooth surface. This technique of surface preparation has been found to give a constant rate of film growth in the process of anodization of specimens under constant current density conditions.

Working area of the specimen: Working area of the specimen was defined by making a thick anodic oxide film (say 250V) on tag in 0.1N citric acid at room temperature. Some oxide layer was always formed on the square portion of specimen surface due to creeping of electrolyte during the formation of film on tag. This extra layer formed was removed by dipping square portion of the sample in KOH melt up to required depth only. The square portion was washed, chemically polished and placed in boiling water as described earlier. In this way, no anodization on tag took place during anodic oxidation of electrode and working area was exactly 2cm².

Experimental set up for anodic polarization: Tantalum specimens prepared by above mentioned procedure were placed in a Pyrex glass cells of diameter 8cm and height 15cm. The specimen was placed in the centre of circular Pt wire mesh which acts as a cathode during anodic oxide film formation. The cell was immersed in a constant temperature thermostat which controlled the temperature up to ±0.05K.

Procedure for anodic growth of oxide film on tantalum: Anodic growth of oxide film on Ta specimen was carried out at constant current. The current was adjusted through an electronically operated constant current generator (General Electronics, Ambala Cantt, India). Electrolysis was terminated by an electronic control after the desired voltage of formation was reached. The time for the passage of current was recorded by an electronic timer (ET 5302, Electronic Corporation of India Ltd., Hyderabad) which could record ±0.1s. Succinic acid used for the formation of anodic oxide films was of analytical grade (Aldrich chemical company, U.S.A.). The steady state kinetic studies of anodic oxide film on tantalum was carried out at

various current densities (2.5, 5.0, 10.0 and 15.0 mAcm⁻²) in 0.1N succinic acid (prepared in 1:1v/v of ethanol + water) solutions at four different temperatures (288.15, 298.15, 308.15 and 318.15K).

Determination of thickness of oxide film: The thickness of Ta film was determined using Faraday's Law as follows:

$$d = \frac{MQ}{10\rho FA} \quad (1)$$

Where: M is gram molecular weight of Ta₂O₅ film, Q is amount of charge passed, ρ is the density of oxide film, F is Faraday's constant and A is area of the specimen. The density of Ta₂O₅ was taken to be 7.93 g·cm⁻³ as reported by Young¹⁶. The value of factor M/10ρFA for Ta₂O₅ films was found to be 2.88664×10⁻⁷ C⁻¹m. The field strength (E = V/d) was calculated at different current density from the calculated thickness of the film and the corresponding voltage of formation.

Results and Discussion

Data for anodic oxidation of Tantalum in succinic acid at various temperatures and current densities have been presented in table-1. The variation of voltage of formation versus charge at 288.15K and at different current densities in 0.1N succinic acid is presented in figure-1.

The rate of growth of oxide film at different current densities and temperatures was found uniform up to 160V in succinic acid. During the growth, color of the film changed at various voltages from purple, fuchsia, turquoise, green and cobalt blue. The dark grey colour and rough surface was observed at the breakdown voltage. It may be due to some local crystallization of Ta₂O₅^{25, 26}.

It was observed that the thickness of the oxide layer governs the color perceived. Thin film interference is responsible for the color. The oxide is transparent and has a high refractive index. Light waves bounce off the oxide, but some go through and reflect off the metal below, reappearing at the surface after a time delay that depends on the thickness of the oxide layer. Those two sets of wave either interfere with or reinforce each other, creating the color to be visible¹⁷. The oxide film itself is resistant to the passage of current and growth of film stops after achieving certain thickness. The linear behavior in voltage versus current plots as shown in figure-1 up to 160V shows that the field strength within film is constant and does not vary significantly with the film thickness.

Plots of field strength E against reciprocal of absolute temperature (figure-2) at different current densities is again linear and parallel and has slope ∂E/∂(1/T). This graph showed that at the same current density, with the rise of temperature, the value of field strength E decreased. A slight scattering of points may be due to the uncertainties involved in the measurements of temperature, current density and pre-history of the film.

Table-1
Anodic growth of oxide film on Ta in 0.1N succinic acid at various temperatures and current densities

Voltage (V)	Charge (C) × 10 ³	Field V/cm × 10 ⁻⁶	Charge (C) × 10 ³	Field V/cm × 10 ⁻⁶	Charge (C) × 10 ³	Field V/cm × 10 ⁻⁶	Charge (C) × 10 ³	Field V/cm × 10 ⁻⁶
Current density								
2.5 mAcm⁻²			5.0 mAcm⁻²		10.0 mAcm⁻²		15.0 mAcm⁻²	
Temperature: 288.15K								
20	91	7.62	86	8.04	82	8.46	78	8.86
40	188	7.38	179	7.74	170	8.13	162	8.56
60	285	7.30	278	7.70	259	8.02	244	8.52
80	382	7.26	363	7.64	349	7.94	328	8.46
100	483	7.18	456	7.61	441	7.86	417	8.32
120	586	7.10	549	7.58	538	7.74	505	8.24
140	684	7.10	637	7.58	637	7.62	594	8.17
160	805	6.90	733	7.57	730	7.60	684	8.12
Temperature: 298.15K								
20	92	7.50	87	7.90	82	8.39	78	8.86
40	192	7.21	184	7.52	173	8.02	163	8.47
60	290	7.16	279	7.46	262	7.94	249	8.34
80	395	7.06	376	7.38	353	7.86	336	8.26
100	505	6.87	474	7.32	446	7.78	426	8.14
120	618	6.74	577	7.21	539	7.72	516	8.06
140	758	6.71	684	7.10	635	7.65	612	7.94
160	831	6.38	799	6.95	733	7.57	706	7.86
Temperature: 308.15K								
20	100	6.94	91	7.60	87	7.95	83	8.34
40	208	6.67	190	7.30	182	7.62	172	8.06
60	316	6.58	287	7.24	275	7.56	259	8.02
80	426	6.52	389	7.14	370	7.50	350	7.92
100	537	6.46	493	7.03	467	7.42	441	7.86
120	653	6.38	597	6.97	566	7.36	535	7.78
140	772	6.29	708	6.85	665	7.30	631	7.70
160	891	6.23	821	6.76	765	7.26	727	7.64
Temperature: 318.15K								
20	104	6.65	94	7.35	91	7.58	87	7.90
40	223	6.21	197	7.04	190	7.28	185	7.67
60	339	6.14	299	6.96	289	7.19	280	7.50
80	455	6.10	406	6.84	391	7.10	376	7.44
100	571	6.08	516	6.72	491	7.06	472	7.38
120	699	5.96	623	6.68	598	6.96	572	7.32
140	821	5.92	735	6.61	698	6.96	675	7.28
160	948	5.86	854	6.50	802	6.92	773	7.18

The data presented in table-2 has been analyzed by considering various theories for ionic conduction. Applying the Guntherschulze and Betz empirical equation, constants A and B were calculated by using the method of least squares and tabulated in table-3. The validity of this equation was verified at various current densities. Though the value of A varied with temperature but the value of B is found almost independent of temperature. This implies the non-dependence of the Tafel slope on temperature.

Table-2
Mean fields at different current densities and temperatures in 0.1N succinic acid

Current Density (mAcm ⁻²)	Field (E) at various temperatures × 10 ⁶ Vcm ⁻¹			
	288.15K	298.15K	308.15K	318.15K
2.5	7.20	6.82	6.48	6.11
5.0	7.70	7.36	7.08	6.68
10.0	8.21	7.82	7.52	7.16
15.0	8.55	8.18	7.86	7.46

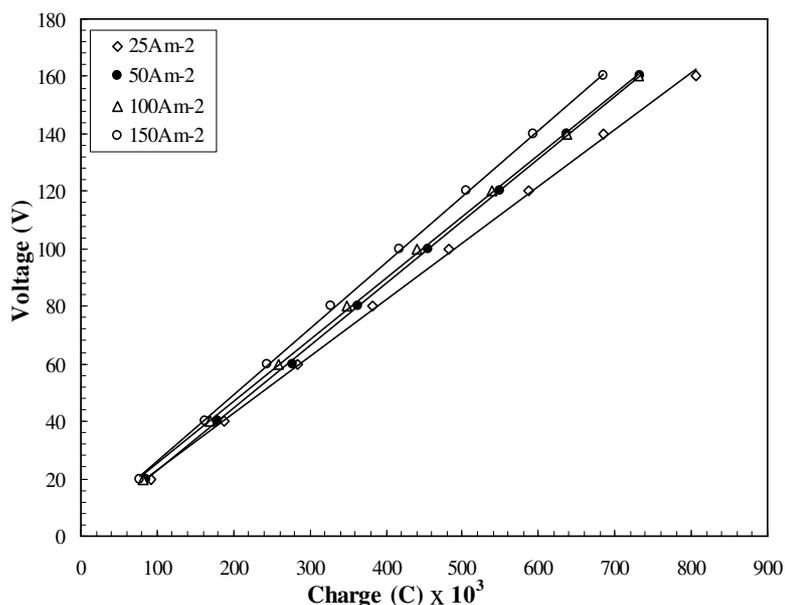


Figure-1

Variation in voltage of formation with charge passed at different current densities at 288.15K (\diamond – 25Am⁻², \bullet – 50Am⁻², Δ – 100Am⁻², \circ – 150Am⁻²)

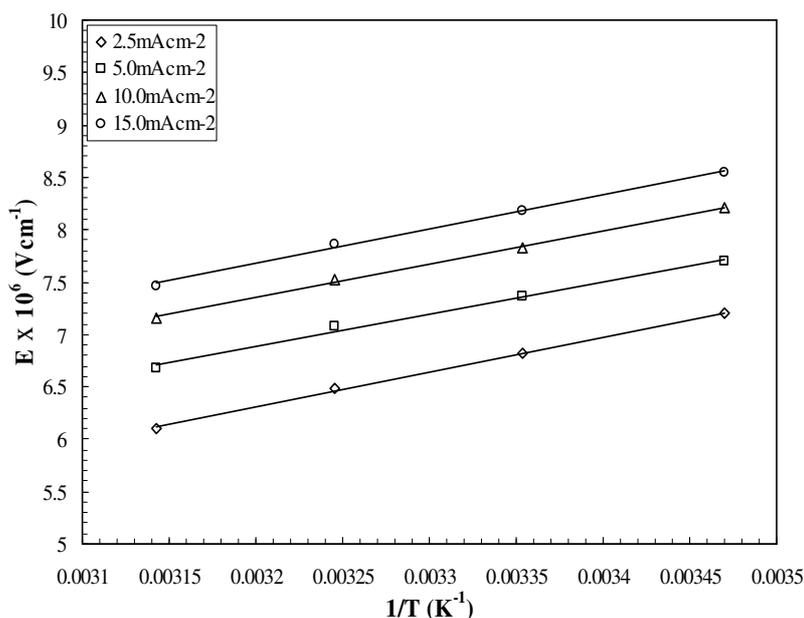


Figure-2

Plot of E vs 1/T at different current density sets, (\diamond – 25Am⁻², \square – 50Am⁻², Δ – 100Am⁻², \circ – 150Am⁻²)

According to the single barrier theory of Cabrera and Mott for ionic growth, E is given by⁸:

$$E = \frac{kT}{bq} \ln \left(\frac{i}{N_s v_s q} \right) + \frac{\phi}{bq} \quad (2)$$

Where, all the terms have their usual significance⁸. According to

single barrier theory, the Tafel slope ($\partial E / \partial \ln i$) is dependent on temperature. The value of Tafel slope is directly proportional to the absolute temperature. However, the values of Tafel slope obtained from the graph plotted between E and $\ln i$ (figure-3) at different temperatures are found constant. It is therefore, the applicability of this theory was ruled out.

Table-3
Parameters of Guntherschulze-Betz equation in 0.1N succinic acid at different temperatures

Temperature (K)	A Acm ⁻²	B cmV ⁻¹
288.15	1.42×10 ⁻⁷	1.36×10 ⁻⁶
298.15	1.94×10 ⁻⁷	1.38×10 ⁻⁶
308.15	2.20×10 ⁻⁷	1.43×10 ⁻⁶
318.15	8.80×10 ⁻⁷	1.37×10 ⁻⁶

Dignam attempted to explain the field and temperature dependence of Tafel slopes for steady state anodic oxidation of valve metals by considering a simple model, according to which the field independent component of potential energy function for displacement of a mobile charged species was assumed to resemble a Morse function¹¹. According to this model, steady state data for anodic oxidation for these metals were represented by three empirical constants; the exponential factor, the activation energy and Morse function distance parameter. According to him at high fields, the relation between current density and field strength was given by¹¹:

$$i = i_0 \exp\left(\frac{-\{\phi - \mu^* E(1 - (\mu^* E / C\phi))\}}{kT}\right) \quad (3)$$

Where, i_0 is the primary current density, ϕ is the zero field activation energy, C is a dimensionless quantity and μ^* is the zero field activation dipole. Parameters μ^* , ϕ and C are not independent constants but are related through the form of potential energy function¹¹. equation-3 may be written as:

$$E = \frac{C\phi}{2\mu^*} \left[1 - \left\{ 1 - \frac{4}{C} - \frac{4kT}{C\phi} \ln\left(\frac{i}{i_0}\right) \right\}^{\frac{1}{2}} \right] \quad (4)$$

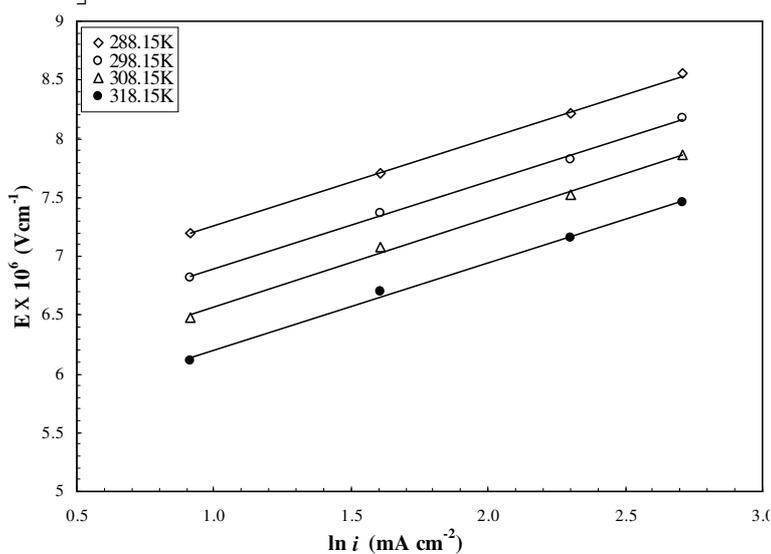


Figure-3
Variation of field (E) with ln i at different temperatures, (◇ – 288.15K, ○ – 298.15K, Δ – 308.15K, ● – 318.15K)

Also,

$$\frac{\partial E}{\partial(1/T)} = S = - \left[\frac{kT^2}{\mu^*} \ln\left(\frac{i}{i_0}\right) \right] \left[1 - \frac{4}{C} - \frac{4kT}{C\phi} \ln\left(\frac{i}{i_0}\right) \right]^{\frac{1}{2}} \quad (5)$$

If $\partial S / \partial \ln i = 0$, that is, Tafel slope being temperature independent, we have from equation-5:

$$C = 4 + \frac{2kT}{\phi} \ln\left(\frac{i}{i_0}\right) \quad (6)$$

The reciprocal of Tafel slope, is given by

$$\beta = \frac{\partial \ln i}{\partial E} = \frac{\mu^*}{kT} \left(1 - \frac{2\mu^* E}{C\phi} \right) \quad (7)$$

Various parameters of Dignam's equation can be solved using above equation as follows:

$$C = 4 \left[1 + \left(1 + \frac{TE}{S} \right)^2 \right]^{-1} \quad (8)$$

$$\mu^* = \left(1 + \frac{TE}{S} \right) kT\beta \quad (9)$$

$$\frac{\mu^* E}{C\phi} = \frac{1}{2} \left(1 + \frac{S}{TE} \right)^{-1} \quad (10)$$

The values of μ^* , C and ϕ were calculated from equations- 8, 9 and 10 at different current densities as a function of temperature in the presence of aqueous succinic acid and are reported in table-4.

Table-4
Various parameters calculated from the Dignam's model

Parameter	Current Density (mAcm ⁻²)	Temperature (K)			
		288.15	298.15	308.15	318.15
μ^* (eÅ)	2.5	5.40	5.79	6.67	7.17
	5.0	5.55	5.93	6.90	7.43
	10.0	5.70	6.12	7.01	7.63
	15.0	5.80	6.23	7.15	7.71
C	2.5	2.94	2.93	2.82	2.81
	5.0	2.98	2.97	2.87	2.84
	10.0	3.00	3.01	2.94	2.90
	15.0	3.05	3.04	2.96	2.95
ϕ (eV)	2.5	0.683	0.680	0.767	0.842
	5.0	0.712	0.717	0.813	0.887
	10.0	0.73	0.738	0.913	0.922
	15.0	0.76	0.762	0.920	0.937
w^* (eÅ)	2.5	1.09	1.12	1.13	1.25
	5.0	1.15	1.15	1.23	1.37
	10.0	1.22	1.22	1.28	1.45
	15.0	1.28	1.28	1.34	1.49
log i_0	2.5	11.85	11.65	11.55	11.43
	5.0	12.00	11.85	11.66	11.49
	10.0	12.21	12.17	12.15	12.13
	15.0	12.42	12.31	12.26	12.22

The values of zero field charge-activation distance product (μ^*) are found to increase with the temperature as well as the current density. Temperature has negligible effect on the magnitude of quadratic parameter (C) and zero field activation energy (ϕ) but they depend slightly on nature of aqueous electrolyte. The quantities C as well as ϕ both increase marginally with the current density. The dependence of μ^* and ϕ with the current density were not observed by Dignam due to non-availability of steady state data for a wide range of temperature and current density.

The equation of ionic conduction can also be written as¹³:

$$i = i_0 \exp \left[- \left\{ \frac{\phi - w^* E (1 - \ln(w^* E / 2\phi)) - (w^* E / 2\phi)}{kT} \right\} \right] \quad (11)$$

Where: w^* is the Morse function parameter and has the same dimensions as μ^* and is given by

$$\frac{w^* E}{\phi} = \left\{ 1 + \frac{2}{C} \left(\frac{\mu^* E}{\phi} \right)^2 \right\}^{\frac{1}{2}} - 1 \quad (12)$$

The values of w^* are calculated using the values of E, μ^* , C and ϕ are found dependent on the temperature and the current density.

The net activation energy W(E) values were calculated as follows:

$$W(E) = \phi - \mu^* E \left(1 - \frac{\mu^* E}{C\phi} \right) \quad (13)$$

The value of W(E) is found to be 0.82 for aqueous succinic acid. The value of W(E) is found to be independent of temperature as well as current density. The quantity $\mu^* E / C\phi$ measures the extent of the contribution of the quadratic term over the entire range of data and was found to be 14-16%.

From equation-3 and 13:

$$i = i_0 \exp \left(\frac{-W(E)}{kT} \right) \quad (14)$$

The values of i_0 were calculated using equation- 14. The ln i_0 values are found to be temperature dependent in contrast to the assumption of Dignam model. The values of i_0 were found to change with the current density. It appears that increase in temperature causes increase in activation distance product (μ^*). This explains the increase of w^* with temperature. As ϕ and W(E) are the activation energies, therefore they are not affected by temperature. The increase in value of μ^* and w^* with current density may be due to mobile ions. The parameters i_0 and C have no dimensions; hence they are not affected by temperature and current density. While deriving above equations, it was supposed that the overall rate of growth of anodic oxide film is controlled solely by the high field transfer of one kind of ionic species. The rate controlling step may be either at the interface or within the film. The space charge contribution was assumed to be zero. The variation of Morse function parameters with temperature and current density explicitly indicate that single barrier theory is not applicable in the present study. It may be due to the existence of space charge in anodic oxide films.

Conclusion

In brief, high field ionic conduction in anodic oxide film on tantalum has been examined at various current densities and temperatures in presence of 0.1N succinic acid. The constants A and B of Guntherschulze and Betz empirical equation have been determined. The value of B was found independent of temperature, which implies the non-dependence of Tafel slope on temperature. Various parameters of Dignam model i.e. zero field activation energy (ϕ), dimensionless quantity (C), zero field activation dipole (μ^*), net activation energy W(E) and Morse function parameter (w^*) have been evaluated and the effects of temperature and current density on these parameters have been discussed.

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