Available online at www.scholarsresearchlibrary.com

Scholars Research Library

European Journal of Applied Engineering and Scientific Research, 2013, 2 (1):25-35
(http://scholarsresearchlibrary.com/archive.html)

ISSN: 2278 – 0041

High field ionic conduction in anodic oxide films on tantalum in aqueous electrolytes

Hariom, Naveen Verma *, Krishan Chander Singh

Department of Chemistry, Maharshi Dayanand University, Rohtak, India

ABSTRACT

The studies on the anodic growth of film on tantalum were carried out at various current densities (2.5, 5.0, 10.0 and 15.0 mAcm^{-2}) in presence of 0.1N solutions of acetic acid, succinic acid and picric acid (prepared in 1:1v/v of Ethanol + water) at four different temperatures (288.15, 298.15, 308.15 and 318.15K). The constants A and B of Guntherschulze and 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. Dignam's quadratic variation of field strength with ionic current density was examined critically. The zero field activation energy (ϕ), dimensionless quantity (C), zero field activation dipole (μ^*), net activation energy W (E) and More function parameter (w^*) of Dignam model were evaluated. The effects of temperature, current density and nature of electrolyte on various parameters of Dignam model have been discussed. An appreciable contribution of the quadratic term elucidates that single-barrier theories of ionic conduction do not explain the data satisfactorily.

Keywords: Anodic oxidation; Tantalum; Tafel slope; Dignam model

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 three methods (i) galvanostatically (ii) potentiostatically and (iii) by a sequence of constant current and constant voltage.

Anodic oxidation of valve metal plate in an acidic aqueous 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 technology [1-2]. The high dielectric constant [3] and high breakdown potential make these anodic oxide films particularly useful in the industrial chemical processes [4] related to electronic devices, batteries, thin film transistors, corrosion protection films, fuel cells, thin film devices, nuclear technology [5], rectifiers and in capacitor technology [6] as dielectric, marine engineering [7] and insulating materials. Ta_2O_5 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 growth of films on valve metals for a long time have been interpreted in terms of high field ionic conduction equation i = A exp(BE), where i is current density, E is the electric field strength in the film and A and B are positive temperature dependent constants. This relation is also known as Guntherschulze-Betz equation [8]. Various other models have been proposed to explain the growth kinetics but divergent views have been expressed by different workers [9-29]. According to Cabrera and Mott [9-10], the Tafel slope should be proportional to temperature. However, Young [15-18], Vermilyea and others [20] found Tafel slope to be independent of temperature. Young [15] and Dignam [13] took into account the quadratic variation of field with ionic current density to explain the field and temperature dependence of Tafel slope. It appears that the exact behavior of Tafel slope with temperature needs 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 different media at a wide range of temperatures and current densities has been investigated. The behavior of Tafel slope and critical assessment of various ionic conduction theories with special reference to Dignam's approach has been made.

MATERIALS 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.

1. Technique for the preparation of surface of specimen for anodic polarization

Square tantalum samples (2cm^2 in area) 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% H_2SO_4, 70% HNO_3 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.

2. 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 2cm^2.

3. 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.

4. Procedure for anodic growth of oxide film on tantalum

Anodic polarization of Ta specimen was carried out at constant current 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 for forming oxide film through successive interval of voltage was recorded by an electronic timer (ET 5302, Electronic Corporation of India Ltd., Hyderabad) which could record ±0.1s. The chemical compounds for the formation of anodic oxide films were 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 acetic acid, 0.1N

succinic acid and 0.1N picric acid (prepared in 1:1v/v of Ethanol + water) solutions at four different temperatures (288.15, 298.15, 308.15 and 318.15K).

5. Determination of thickness of oxide film

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

$$d = MQ/10\rho FA \quad (1)$$

where M is gram molecular weight of Ta_2O_5 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 Ta_2O_5 was taken to be 7.93 gcm^{-3} as reported by Young [21]. The value of factor M/10ρFA for Ta_2O_5 films was found to be 2.88664×10^{-7} $C^{-1}m$. Using the calculated thickness of the film and the corresponding voltage of formation, the field strength (E = V/d) was calculated at any given current density.

RESULTS AND DISCUSSION

Data for anodic oxidation of Tantalum in acetic, succinic and picric 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 Fig. 1. Similar plots were also obtained at other temperatures i.e. 298.15, 308.15 and 318.15K and other electrolytes i.e. acetic acid and picric acid.

The rate of growth of oxide film at different current densities and temperatures was found uniform up to 160V in acetic, succinic and picric acid. During the growth, color of the film changed at various voltages from purple, fuchsia, turquoise, green and cobalt blue. At the breakdown voltage [30] the color was dark grey and the surface was rough; this may be due to some local crystallization of Ta_2O_5 [31].

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 visible [22]. The oxide film itself is resistant to the passage of current and grows to a certain thickness and then stops. The linear behavior in voltage versus current plots as shown in Fig. 1 up to 160V shows that the field strength within film is constant and is almost independent of film thickness.

Plots of field strength E against reciprocal of absolute temperature (Fig. 2) at different current densities is again linear and parallel and have 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: Formation of anodic oxide film on tantalum in aqueous electrolytes at various temperatures and at different current densities.

Voltage Volts	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 mA cm^{-2}		5.0 mA cm^{-2}		10.0mA cm^{-2}		15.0mA cm^{-2}	
Electrolyte: 0.1N Succinic Acid								
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	254	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

Electrolyte: 0.1N Acetic Acid

Temperature: 288.15K								
20	97	7.14	90	7.70	86	8.06	82	8.45
40	195	7.10	184	7.53	174	7.97	166	8.36
60	297	7.00	281	7.40	262	7.93	2.55	8.14
80	396	6.96	378	7.34	353	7.86	344	8.06
100	498	6.93	474	7.32	448	7.74	433	8.01
120	601	6.92	572	7.28	546	7.62	523	7.96
140	704	6.90	671	7.24	644	7.54	613	7.92
160	809	6.86	780	7.12	744	7.46	708	7.84
Temperature: 298.15K								
20	97	7.14	94	7.37	90	7.70	85	8.16
40	207	6.70	194	7.15	188	7.38	179	7.75
60	314	6.62	298	6.97	286	7.28	273	7.62
80	424	6.54	404	6.86	382	7.26	367	7.56
100	535	6.48	507	6.84	479	7.24	461	7.52
120	643	6.48	616	6.76	578	7.20	557	7.48
140	757	6.42	712	6.74	678	7.16	651	7.46
160	873	6.36	826	6.72	784	7.08	752	7.38
Temperature: 308.15K								
20	103	6.73	96	7.22	90	7.64	87	7.92
40	221	6.28	206	6.74	183	7.18	188	7.36
60	322	6.46	310	6.70	295	7.06	286	7.28
80	449	6.18	415	6.68	400	6.94	387	7.16
100	572	6.07	523	6.63	505	6.87	493	7.04
120	697	5.97	637	6.52	616	6.76	598	6.96
140	821	5.92	757	6.42	719	6.76	710	6.84
160	943	5.86	870	6.38	831	6.68	826	6.72
Temperature: 318.15K								
20	107	6.47	102	6.75	96	7.16	92	7.50
40	227	6.10	219	6.32	206	6.72	193	7.18
60	349	5.96	330	6.30	313	6.64	301	6.92
80	467	5.94	445	6.24	426	6.52	404	6.86
100	592	5.86	561	6.18	537	6.46	509	6.82
120	713	5.84	689	6.04	651	6.40	618	6.74
140	814	5.78	804	6.04	764	6.36	732	6.64
160	983	5.76	932	6.01	884	6.28	852	6.52

Contd…….

Electrolyte: 0.1N Picric Acid

				Temperature: 288.15K				
20	97	7.14	87	7.96	82	8.42	77	8.44
40	203	6.84	179	7.74	175	7.92	166	8.32
60	305	6.81	271	7.68	263	7.90	252	8.26
80	409	6.78	367	7.56	354	7.84	341	8.14
100	515	6.74	464	7.48	445	7.80	430	8.06
120	623	6.68	561	7.42	538	7.74	522	7.97
140	734	6.62	658	7.38	632	7.69	613	7.92
160	846	6.60	765	7.26	724	7.67	708	7.84
				Temperature: 298.15K				
20	99	6.98	92	7.54	86	8.06	81	8.50
40	207	6.68	198	7.34	181	7.64	170	8.14
60	314	6.62	286	7.26	274	7.60	263	7.92
80	422	6.58	385	7.20	367	7.56	353	7.86
100	533	6.51	484	7.16	462	7.50	448	7.74
120	644	6.46	591	7.04	557	7.48	541	7.70
140	761	6.38	698	6.96	656	7.40	632	7.68
160	879	6.32	812	6.84	754	7.36	729	7.62
				Temperature: 308.15K				
20	102	6.78	94	7.36	89	7.78	85	8.02
40	215	6.45	196	7.06	185	7.48	179	7.72
60	325	6.40	200	6.93	280	7.42	271	7.67
80	436	6.36	404	6.86	378	7.34	364	7.62
100	551	6.30	509	6.82	482	7.20	459	7.56
120	665	6.26	616	6.76	586	7.10	555	7.50
140	791	6.14	723	6.72	688	7.06	651	7.46
160	907	6.12	795	6.98	786	7.06	748	7.42
				Temperature: 318.15K				
20	108	6.42	101	6.85	94	7.32	89	7.76
40	217	6.38	206	6.72	187	7.24	182	7.62
60	330	6.30	311	6.69	290	7.16	284	7.32
80	442	6.28	419	6.62	394	7.04	381	7.28
100	567	6.12	530	7.54	500	6.94	482	7.20
120	692	6.02	655	6.36	607	6.86	581	7.16
140	815	5.96	774	6.28	715	6.79	686	7.08
160	954	5.82	894	6.21	824	6.74	791	7.02

Table 2: Mean fields at different current densities and temperatures in various aqueous electrolytes

Current Density (mA cm^{-2})	**Field (E) at various temperatures** $\times 10^6$ Vcm^{-1}			
	288.15K	**298.15K**	**308.15K**	**318.15K**
Electrolyte: 0.1N Acetic Acid				
2.5	6.92	6.50	6.12	5.80
5.0	7.25	6.92	6.56	6.20
10.0	7.52	7.25	6.90	6.56
15.0	7.92	7.52	7.13	6.80
Electrolyte: 0.1N Succinic Acid				
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
Electrolyte: 0.1N Picric Acid				
2.5	6.87	6.51	6.32	6.12
5.0	7.40	7.15	6.84	6.52
10.0	7.86	7.52	7.25	7.02
15.0	8.22	7.83	7.61	7.23

Table 3: Values of parameters A and B of Guntherschulze and Betz equation for various aqueous electrolytes at different temperatures

Temperature (K)	A Acm^{-2}	B cmV^{-1}
Electrolyte: 0.1N Acetic Acid		
288.15	1.0×10^{-8}	1.778×10^{-6}
298.15	2.0×10^{-8}	1.798×10^{-6}
308.15	4.0×10^{-8}	1.798×10^{-6}
318.15	6.9×10^{-8}	1.808×10^{-6}
Electrolyte: 0.1N Succinic Acid		
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}
Electrolyte: 0.1N Picric Acid		
288.15	1.56×10^{-7}	1.395×10^{-6}
298.15	2.58×10^{-7}	1.398×10^{-6}
308.15	3.06×10^{-7}	1.424×10^{-6}
318.15	1.35×10^{-7}	1.602×10^{-6}

Table 4: Values of different parameters calculated from the Dignam's ionic conduction equations.

Para- meter	Current Density $mAcm^{-2}$	Temperature			
		288.15K	**298.15K**	**308.15K**	**318.15K**
Electrolyte: 0.1N Succinic Acid					
	2.5	5.40	5.79	6.67	7.17
μ^* (e^oA)	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
	2.5	2.94	2.93	2.82	2.81
C	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
	2.5	0.683	0.680	0.767	0.842
ϕ (eV)	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
	2.5	1.09	1.12	1.13	1.25
w^* (e^oA)	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
	2.5	11.85	11.65	11.55	11.43
log i_o	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
Electrolyte: 0.1N Acetic Acid					
	2.5	6.78	7.04	7.20	7.57
μ^* (e^oA)	5.0	7.00	7.21	7.38	7.76
	10.0	7.12	7.34	7.53	7.92
	15.0	7.22	7.45	7.62	8.04
	2.5	2.87	2.84	2.83	2.82
C	5.0	2.91	2.88	2.87	2.86
	10.0	2.94	2.91	2.90	2.89
	15.0	2.96	2.94	2.93	2.92
	2.5	0.86	0.88	0.87	0.88
ϕ (eV)	5.0	0.90	0.91	0.90	0.91
	10.0	0.93	0.93	0.93	0.94
	15.0	0.95	0.95	0.94	0.95
	2.5	1.22	1.23	1.24	1.58
w^* (e^oA)	5.0	1.30	1.31	1.32	1.78
	10.0	1.34	1.37	1.38	1.84
	15.0	1.38	1.42	1.43	1.92
	2.5	17.2	17.1	16.5	16.3
log i_o	5.0	17.3	17.4	16.7	16.5
	10.0	17.8	17.5	17.2	16.8

	15.0	18.1	17.6	17.4	16.9
Electrolyte: 0.1N Picric Acid					
	2.5	5.98	6.37	6.86	7.48
μ^* (e°A)	5.0	6.24	7.26	7.58	7.81
	10.0	6.34	7.46	7.75	8.03
	15.0	6.46	7.57	7.91	8.13
	2.5	2.90	2.98	3.00	3.01
C	5.0	2.94	3.05	3.08	3.06
	10.0	2.97	3.11	3.09	3.10
	15.0	3.00	3.14	3.15	3.16
	2.5	0.729	0.708	0.685	0.665
ϕ (eV)	5.0	0.780	0.744	0.690	0.678
	10.0	0.796	0.772	0.712	0.694
	15.0	0.820	0.794	0.725	0.7.06
	2.5	1.10	1.41	1.42	1.43
w^* (e°A)	5.0	1.21	1.46	1.48	1.55
	10.0	1.26	1.60	1.61	1.64
	15.0	1.30	1.66	1.68	1.70
	2.5	11.3	11.0	9.37	9.12
log i_o	5.0	11.6	11.0	9.75	9.55
	10.0	11.7	11.35	10.16	9.94
	15.0	11.8	11.4	10.16	10.04

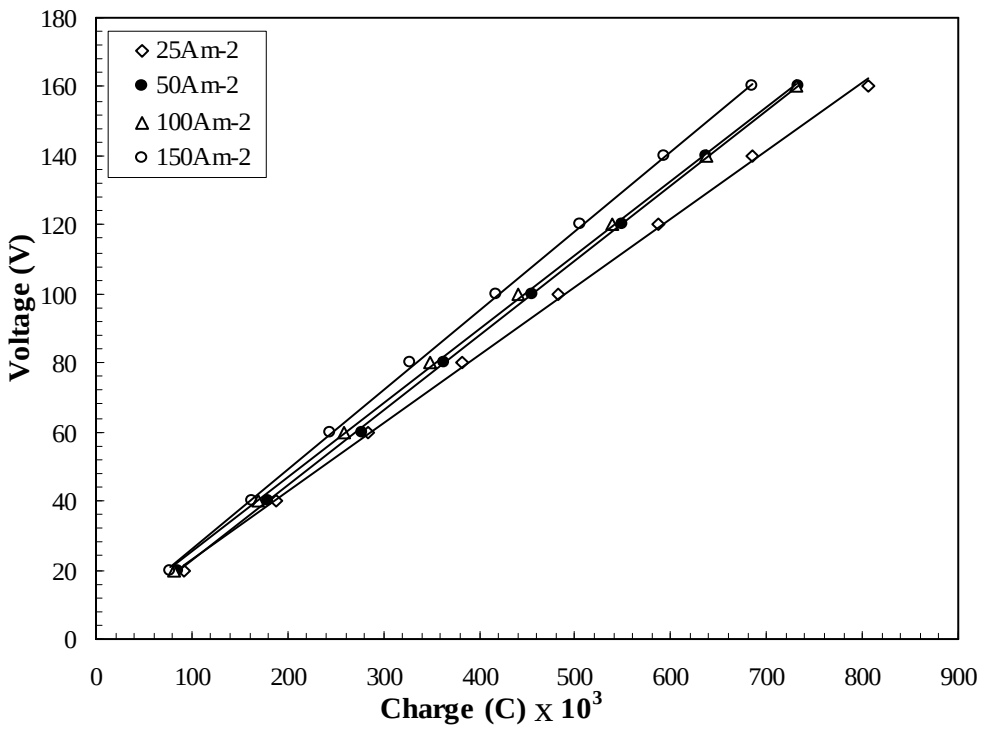

Fig. 1. Variation in voltage of formation with charge passed at 288.15K and different current densities (Electrolyte = 0.1N succinic acid, ◊ – 25Am^{-2}, ● – 50Am^{-2}, Δ –100Am^{-2}, ○ –150Am^{-2}).

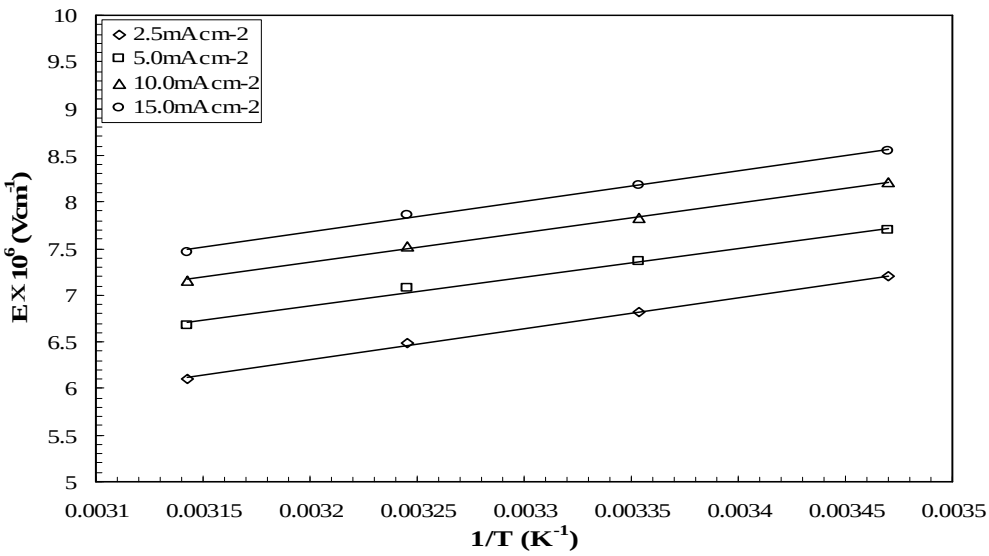

Fig. 2. Plot of E vs 1/T at different current density sets (Electrolyte: 0.1N succinic acid, ◊ -25Am^{-2}, □ – 50Am^{-2}, Δ – 100Am^{-2}, ○ – 150Am^{-2}).

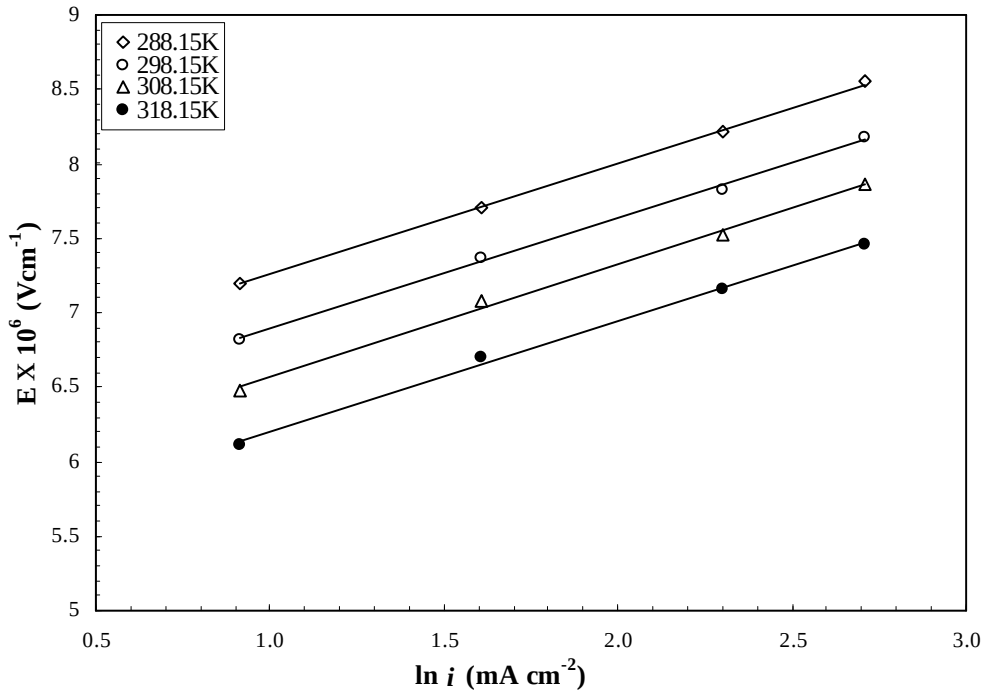

Fig. 3. Variation of field (E) with ln *i* at different temperatures (Electrolyte: 0.1N succinic acid, ◊ – 288.15K, ○ – 298.15K, Δ – 308.15K, ● – 318.15 K)

The data presented in Table 1 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 and for different aqueous electrolytes. The value of A varies with temperature but there is not much significant variation in the values of B, indicating the value of B to be independent of temperature. This implies the non-dependence of Tafel slope on temperature. The value of A and B, however, vary with the nature of the aqueous electrolyte.

According to the single barrier theory of Cabrera and Mott [9,10] for ionic growth, E is given by:

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

where all the terms have their usual significance [9,10]. According to this theory, the Tafel slope ($\partial E/\partial \ln i$) should be directly proportional to absolute temperature. Tafel slope values obtained from the graph between E and ln i (as shown in Fig. 3) at different temperatures are constant, thus the applicability of this theory was ruled out.

Dignam [13,17] attempted to explain the field and temperature dependence of Tafel slopes for steady state anodic oxidation of Ta, Nb and other 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 function. 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 by [13,17]:

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

where i_o 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 function.
Eq. (3) may be written as:

$$E = \frac{C\phi}{2\mu^*}\left[1 - \left\{ 1 - \frac{4}{C} - \frac{4kT}{C\phi} n\left(\frac{i}{i_o} \right) \right\}^{1/2} \right] \tag{4}$$

Also,

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

if $\partial S/\partial \ln i = 0$, that is, Tafel slope being temperature independent, we have from Eq. (5)

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

The reciprocal of Tafel slope, is given by

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

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

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

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

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

The values of μ^*, C and ϕ were calculated from Eq. (8, 9 and 10) at varying current densities as a function of temperature in the presence of all the three electrolytes and are reported in Table 4.

The values of zero field charge-activation distance product (μ^*) are found to increase with temperature as well as the current density. At a particular temperature, values of μ^* are also found dependent on the nature of the electrolyte. 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 and ϕ both increase slightly with current density. The dependence of μ^* and ϕ with the nature of electrolyte and current density were not observed by Dignam due to non-availability of steady state data for a wide range of temperature, current density and electrolyte composition.

The equation of ionic conduction can also be written as[17]:

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

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

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

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

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

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

The values of $W(E)$ are found to be 2.37, 0.82, 0.46 for acetic, succinic and picric acid respectively. The values of $W(E)$ were found to be temperature and current density independent but vary with the nature of electrolyte for all the three acids. 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 (11-13%, 14-16% and 17.5-20%) for acetic, succinic and picric acid respectively.
From Eq. (3) and (13)

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

The values of log i_o were calculated using Eq. (14). The values are found to be temperature dependent and not independent as assumed by Dignam. The values of i_o were found to change with composition of the electrolyte or 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 number of mobile ions vary in different electrolytes and it leads to change in magnitude of μ^* and w^*. The parameters i_o and C have no dimensions, hence they are not affected by temperature and current density. In the derivation of above equations, it was assumed that the overall rate is controlled solely by the high field transfer of one kind of ionic species. The rate controlling step may be at the interface or within the film. The space charge contribution was assumed to be zero. As there is a variation of Morse function parameters with temperature and current density, thus a single barrier theory is not strictly applicable to our data. There might be the possibility of the existence of space charge in such 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 aqueous electrolytes. 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 More function parameter (w^*) have been evaluated and the effects of temperature, current density and nature of electrolyte on these parameters have been discussed.

REFERENCES

[1] Song H. J., Lee C. S. and Kang S. W., *Electrochem. Solid-State Lett.*, **2001**, 4, F13-F14.
[2] EI-Mahdy G. A., *Thin Solid films*, **1997**, 307,141-147.
[3] Kamada K., Mukai M. and Matsumoto Y., *Electrochim. Acta*, **2004**, 49, 321-327.
[4] Smallwood R. E., Use of Refractory Metals in Chemical Process Industries: In Refractory Metals and their Industrial Application, *ASTM, Philadelphia, PA*, **1984**, 106.
[5] Frost B. R. T., Nuclear Fuels Elements: Design, Fabrication and Performance (Pergamon Press, Oxford) **1982**.
[6] Sikula J., Hlavka J., Sedlakova V. and Grmela L. (AVX Corporation), **2003**.
[7] Geld I., Cathodic Protection Anode with Sections Replaceable under Water, *US Pat*., , 3, 718, 570, **1973**.
[8] Guntherschulze A. and Betz H., *Z. Phys.*, **1934**, 92, 367-373.
[9] Mott N F, *Trans. Faraday Soc.*, **1947**, 43, 429-434.
[10] Cabrera N. and Mott N. F., *Rep. Prog. Phys*, **1948**, 12, 163-174.
[11] Diggle W. J, Anodic Oxide and Oxide Films, Vol I (Marcel Dekker, Inc., New York,.) **1972,** p. 92**.**
[12] Dewald J. F., *J. Electrochem. Soc.*, **1955**, 102, 1-6.
[13] Dignam M. J., *J. Electrochem. Soc.*, **1979**, 126, 2188-2195.
[14] Nigam R. K., Singh K. C and Maken S., *Thin Solid Films* , **1987**, 155, 115-124.
[15] Young L., Anodic Oxide Films, Academic Press, New York, **1961**.
[16] Young L., J. *Electrochem. Soc.*, **1963**, 110, 589-594.
[17] Dignam M. J., *Can. J. Chem.*, **1964**, 42, 1155-1164.
[18] Young L., *Proc. Roy. Soc. London* A, **1966**, 258, 496-515.
[19] Kalra K. C., Katyal P. and Singh K. C., *Thin Solid Films*, **1989**, 177, 35-41.
[20] Kalra K. C., Singh K. C. and Singh M., *Thin Solid Films*, 1994, 239, 99-103.
[21] Young L., *Pro. Roy. Soc London*, A, **1958**, 244, 41-53.
[22] Zurer P. S., C & EN's Washington, **2003**.
[23] Alsabet M., Grden M. and Jerkiewicz G, *J. Electroanal. Chem.*, **2006**, 589, 120-127.
[24] Vijh A. K., *Electrochim. Acta*,**1972**, 17, 91-97.
[25] Hukovic M. M. and Grubac Z., *J. Electroanal. Chem.*, **2003**, 556, 167-178.
[26] Poznyak S. K. , Talapin D. V. and Kulak A. I. , *J. Electroanal. Chem.*, **2005**, 579, 299-310.
[27] Mogoda A. S., El-Taib Heakal F. and Ghoneim A. A., *Thin Solid Films*, **1992**, 219, 146-152.
[28] Kotz R., Schnyder B and Barbero C, *Thin Solid Films*, **1993**, 233, 63-68.
[29] Heidelberg A., Rozenkranz C., Schultze J. W., Schapers T. and Staikov G., *Surface Science* , 2005, 597 , 173-180.
[30] Ikonopisov S., *Electrochim. Acta*, **1977**, 22-1077-1082.
[31] Axelrod N. N. and Schwartz N., *J. Electrochem. So.c*, **1969**, 116, 460-465.