

Ionic Conduction and Electrical Breakdown of Anodic Oxide Thin Films on Tantalum in Aqueous Electrolytes

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Abstract

Ionic conduction and electrical breakdown voltage studies of anodic oxide thin films on tantalum in various aqueous electrolytes have been made. The above studies have been made as a function of current densities, concentration and composition of the electrolytes. The results have been obtained by eliminating the difference of film growth caused by different surface conditions. The effect of electrolyte concentration, composition and resistivity on breakdown characteristics has been explained in terms of the Ionopisov's electron injecting avalanche breakdown model. It is observed that during anodic oxidation the anions of the electrolyte get incorporated into the oxide film which increases with the electrolyte concentration. These incorporated anions results in the formation of traps and the traps are in electronic equilibrium with the electrolyte. The electrons are thermally excited continuously from the traps into the conduction band and electronic equilibrium is maintained by the continuous injection of the electrons from the electrolyte. The high field strength accelerates these electrons to very high energy which cause release of secondary electrons, resulting in the multiplication of avalanches and hence breaking the film at a certain voltage. It has been found that of the various methods for identifying breakdown voltage, the appearance of sparking has been found to be a superior method. The exact phenomenon of breakdown voltage during anodic oxidation of thin films has been obtained.

I. Introduction

When an anodic oxide film is formed at constant current density, there is limit of the thickness of the oxide film beyond which the film breaks down. The voltage at which this phenomenon occurs is referred to as the breakdown voltage. The Breakdown voltages have been studied for different valve metals but the results obtained by different workers are at variance^{2,6-11}. Different workers have variously used methods like i) the rapid voltage fluctuation, ii) attainment of maximum voltage, iii) appearance of visible sparking . iv)

occurrence of audible cracking and slowing down of voltage for identifying breakdown voltage (V_B). In view of the conflicting results and the mechanisms about breakdown voltage suggested, the present work was done using anodic oxide films formed on tantalum in different electrolytes of varying concentrations.

II. Materials & Methods

Square tantalum samples with short tags of known area were cut from 99.9% pure tantalum sheets and the edges of the samples were abraded with fine emery paper to make them smooth. The samples after dipping in KOH melt were washed with distilled water and chemically polished by treating with freshly prepared mixture of 48% HF+70% HNO₃+98% H₂SO₄(2:2:5,v/v) for 3-5 sec. and then washed with distilled water. These samples were then placed in boiling water for about 10 minutes to remove any remaining impurities from the surface of the samples of tantalum. The tag of the samples was covered with a thick anodic film in an electrolyte in which further anodisation on square portion of the samples was to be carried out. The samples was thus prepared was placed in a glass cell and was surrounded by a platinum gauze which served as a cathode during the growth of oxide film. The samples was anodized in different electrolyte solutions at a constant current. The current source used during anodisation was an electronically operated constant current supply unit which can cut off current supply as soon as desired voltage of film formation is reached. The experiments under galvanostatic conditions were carried out up to breakdown voltage in aqueous solutions of potassium chloride, sodium tartrate and sodium carbonate. The aqueous solutions were made with conductivity water and the electrolytic resistivities were measured using a digital conductivity bridge All data refer to temperature of 298 K \pm 0.5K. The time for the passage of current for forming film through successive intervals of voltage was recorded by an electronic timer. The density of tantalum oxide film was taken as 7930 kg/m³as reported by Young⁴.

III. Results and discussion

The anodic oxide films were grown on tantalum specimens at a current density of 100 Am⁻²in varying concentrations of potassium chloride, sodium, tartrate and sodium carbonate. The plot of voltage (V) at which the Oxide films were formed against time (t) for which charged was past in aqueous solution of sodium tartrate are shown in Fig. 1. The data for film formation in aqueous potassium chlorirde in different concentrations is given in Table 1. It is difficult to identify electrical breakdown voltage during anodization in various electrolytes. Therefore different criteria to identify electrical breakdown voltage

were examined. These were 1) The voltage at which gas evolution occurs ii) voltage at which rapid fluctuation in voltage starts iii) The voltage at which audible cracking occurs iv) Reaching of maximum voltage v) slowing down of voltage vi) The voltage at which sparking appears. It has been examined that at low current densities (5.0 and 10.0 Am⁻²) increase in the charge passed increases the voltage of formation upto a certain maximum value thereafter any further increase in charge does not lead to change in voltage of formation. Reaching of maximum voltage has been used as one of the criteria to measure breakdown voltage. However, at higher current densities (500 and 1000 Am⁻²) no such maximum voltage is reached, hence this criterion was not accepted as a measure of breakdown voltage Slowing down of voltage which is also one of the criteria to measure breakdown voltage has not been found useful because the rate of slowing down (dV/dt) decreases as the current density increases and ultimately it reaches almost a zero value in the region of voltage of interest. Rapid voltage fluctuation was only occasionally observed. Gas evolution preceded sparking but at low current densities gas evolution took place for a very long time before sparking started. Hence at low current densities gas evolution is also no better than sparking as a criterion for identifying breakdown voltage. Audible cracking occurred at current densities higher than 10Am⁻² and was not easily detectable at low current densities. Appearance of sparking was observed at all the current densities and further at low current densities(5.0 and 10.0Am⁻²), the sparking voltages were close to the maximum voltage, the appearance of sparking was taken as a measure to identify breakdown voltage. The order of sequence of events which took place during the process of breakdown is summarized as under:

At low current densities (5 and 10 Am⁻²). slowing down of voltage: reaching of maximum voltage: gas evolution staying for a longer period and sparking.

At moderate current densities (50 and 100 Am⁻²). slowing down with much less rate: gas evolution staying for a smaller period: sparking and audible cracking .

At high current densities (500 and 1000 Am⁻²) Gas evolution instantaneously leading to sparking: audible cracking.

The variation of breakdown voltage with time at different current densities in aqueous solution of sodium carbonate (Fig.2) and other electrolyte solutions suggest that breakdown voltage is independent of current density at which the films were formed The values of breakdown voltage are not constant for various electrolytes used. (V_B) was found to decrease with increase in electrolyte concentration and the linear plots between breakdown voltage and logarithms of (concentration)⁻¹ (Fig. 3) confirm this conclusion and hence the effect of concentration of electrolyte on breakdown voltage can be represented by an equation of the form

$$V_B = (V_B)_{M^+} + n \log 1/c$$

$(V_B)_M$ is the minimum value of breakdown voltage which will be obtained when $\log 1/c=0$ i.e. $c=1 \text{ mol dm}^{-3}$ and n is a constant with a positive value. The intercepts of plots in fig.3 gave the value of $(V_B)_M$ for aqueous solution of potassium chloride, sodium tartarate and sodium carbonate as 116.67,150.84 and 142V, respectively and the corresponding values of n from the slopes of these curves were 133.33 , 203.33 and 200, respectively. At high electrolyte concentrations large number of ions were available per unit concentration and hence the electrolyte possesses large electrolytic conductivity but low resistivity. The low values of breakdown voltages obtained at high concentrations of the electrolytes (possessing low resistivities) suggest a direct relation between breakdown voltage and resistivity. The effect of electrolytic resistivity (ρ) on breakdown voltage was checked more directly by measuring the resistivities of aqueous solutions.

The breakdown voltage did not vary linearly with resistivity of the electrolyte. However, the plots between V_B and $\log (\rho)$ (Fig. 4) were found to be linear and hence a relation between V_B and (ρ) can be represented by

$$V_B = a + b \log (\rho)$$

Where a and b are constants with positive sign. The values of constant 'a' for potassium chloride, sodium tartarate and sodium carbonate were obtained from the intercepts of the linear plots (Fig.4) and were 67.5 , 370.24 and 344.64, respectively. The corresponding values of 'b' were found to be 75.00 , 297.62 and 267.86, respectively. The effect of field strength on the breakdown voltage was studied. The values of field strength at 298K (current density 100 A/m^2) for 0.1M aqueous solution of potassium chloride, sodium tartarate and sodium carbonate were found to be 5.36 , 6.47 and $5.93 \times 10^8 \text{ Vm}^{-1}$, respectively. The corresponding values of V_B were 215 , 355 and 305V. The values of breakdown voltage in these solutions being so close suggested that V_B is independent of field strength . Breakdown voltage has been found to decrease slightly with increase in temperature and the effect was more at lower electrolyte concentration. Next, the effect of pH on breakdown voltage was examined .It has been found that breakdown voltage in presence of 0.01M and 0.25M aqueous solution of potassium chloride, is 375 and 195V, respectively and corresponding pH value in these solution is 3.61 and 3.62, respectively. Similarly in case of 0.1M and 0.5M aqueous solution of sodium tartarate, V_B is 355 and 240V, respectively and the corresponding pH value in these solutions is 6.18 and 6.59, which showed that breakdown voltage is independent of pH of the solution. It was observed that tantalum samples having varying degree of topography have almost same breakdown voltage values. The values being so close suggests that V_B is non-dependent on the topography of the samples and breakdown voltage is not triggered by conduction through flaws and fissures on surface of the samples.

The breakdown voltage values in 0.05M solutions of sodium tartarate and sodium carbonate were found to be 420 and 410V, respectively (Table 2). These breakdown voltage values being so close suggested that breakdown voltage is only affected by anions of electrolyte solutions.

It is observed that the breakdown voltage results due to conduction of avalanching in the bulk of the anodic film. During that during anodic polarization the anions of the electrolytes provide electrons which get injected into the conduction bands of the oxide film. At a critical voltage, due to high field strength (of the order of 10^8 Vm^{-1}) the electrons acquire very high energy which causes release of secondary electrons by impact ionization, which results in the multiplication of avalanches and breaking of the film.

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Table -1
Variation of voltage of formation with time in different concentrations of aqueous solution of potassium chloride

1.0 mol m ⁻³		10 mol m ⁻³		25 mol m ⁻³		100 mol m ⁻³		250 mol m ⁻³		500 mol m ⁻³	
Voltage (V)	Time (s)	Voltage (V)	Time (s)	Voltage (V)	Time (s)	Voltage (V)	Time (s)	Voltage (V)	Time (s)	Voltage (V)	Time (s)
10	1	10	2	10	2	10	2	10	2	10	2
20	2	20	3	20	3	20	4	20	4	20	4
50	7	50	10	50	9	50	11	50	11	50	10
70	9	70	15	70	13	70	16	70	15	70	15
100	16	100	21	100	21	100	22	100	24	100	23
125	22	125	27	125	26	125	25	125	27	125	28
150	28	150	33	150	32	150	31	150	32	150	33
175	34	175	38	175	38	175	39	175	38	175	-
200	39	200	40	200	44	200	46	200	-	200	-
225	45	225	44	225	49	225	-	225	-	225	-
250	51	250	54	250	56	250	-	250	-	250	-
275	57	275	62	275	61	275	-	275	-	275	-
300	63	300	67	300	72	300	-	300	-	300	-
350	75	350	80	350	-	350	-	350	-	350	-

TABLE-2
Electrical breakdown voltage (V_B) values and electrolytic resistivity for different electrolyte solutions

Concentration (mol m ⁻³)	Potassium Chloride			Sodium Tartarate			Sodium Carbonate		
	Breakdown Voltage (V)	Electrolytic Resistivity (ΩM)	pH	Breakdown Voltage (V)	Electrolytic Resistivity (ΩM)	pH	Breakdown Voltage (V)	Electrolytic Resistivity (ΩM)	pH
50	245	185.19	3.61	420	1.54	5.93	410	1.35	11.07
100	215	90.99	3.60	355	0.91	6.18	305	0.77	11.19
200	200	57.14	3.61	290	0.57	6.44	280	0.59	11.23
250	195	46.51	3.62	270	0.48	6.56	255	0.45	11.25
300	190	40.82	3.65	260	0.44	6.57	235	0.35	11.29
500	170	28.57	3.63	240	0.33	6.59	180	0.24	11.32

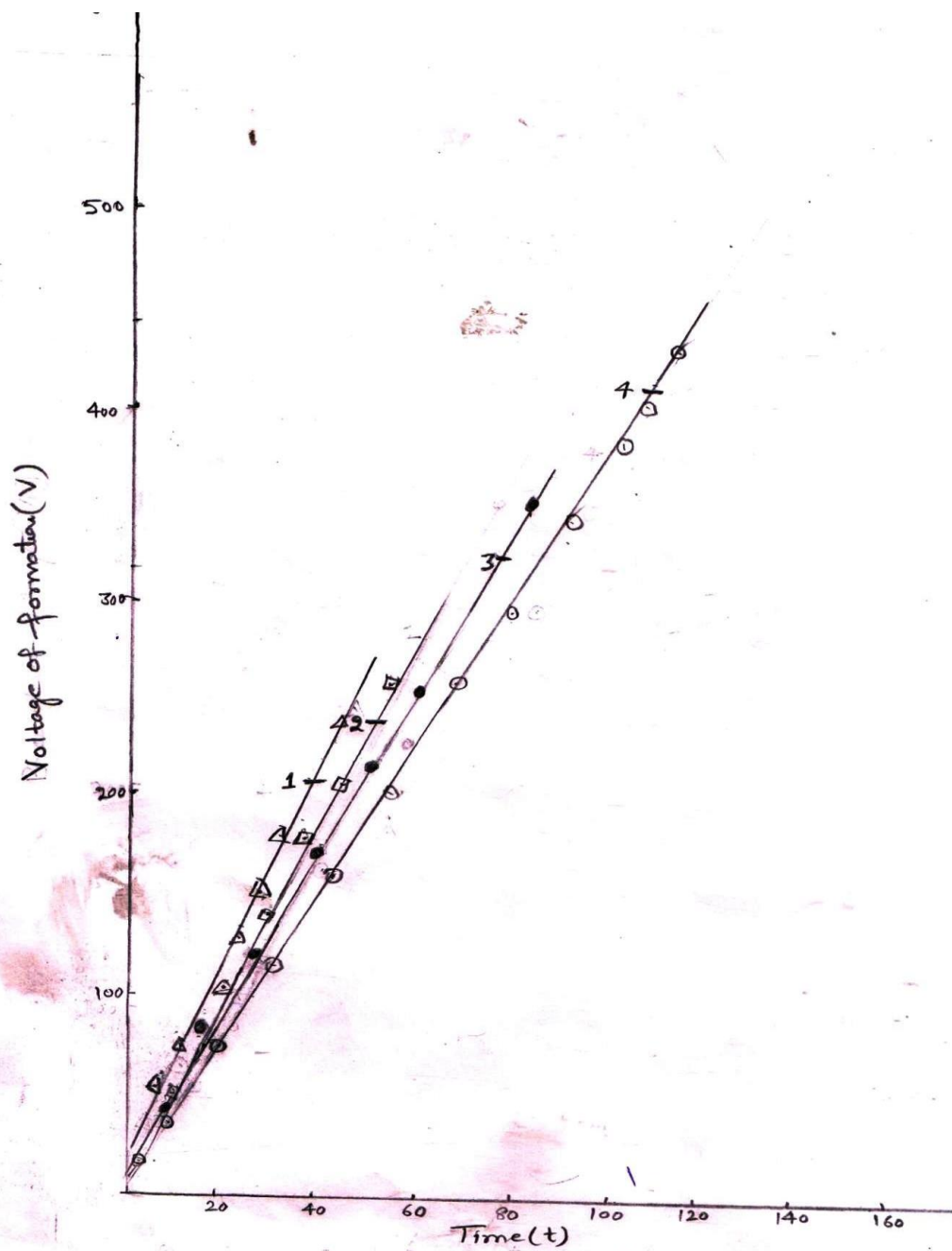


Fig. 1. Variation of Voltage formation with time at different concentrations in aqueous sodium tartarate. [o] 50 mol m⁻³; (●) 100 mol m⁻³; . 250 mol m⁻³; □ 500 mol m⁻³ △

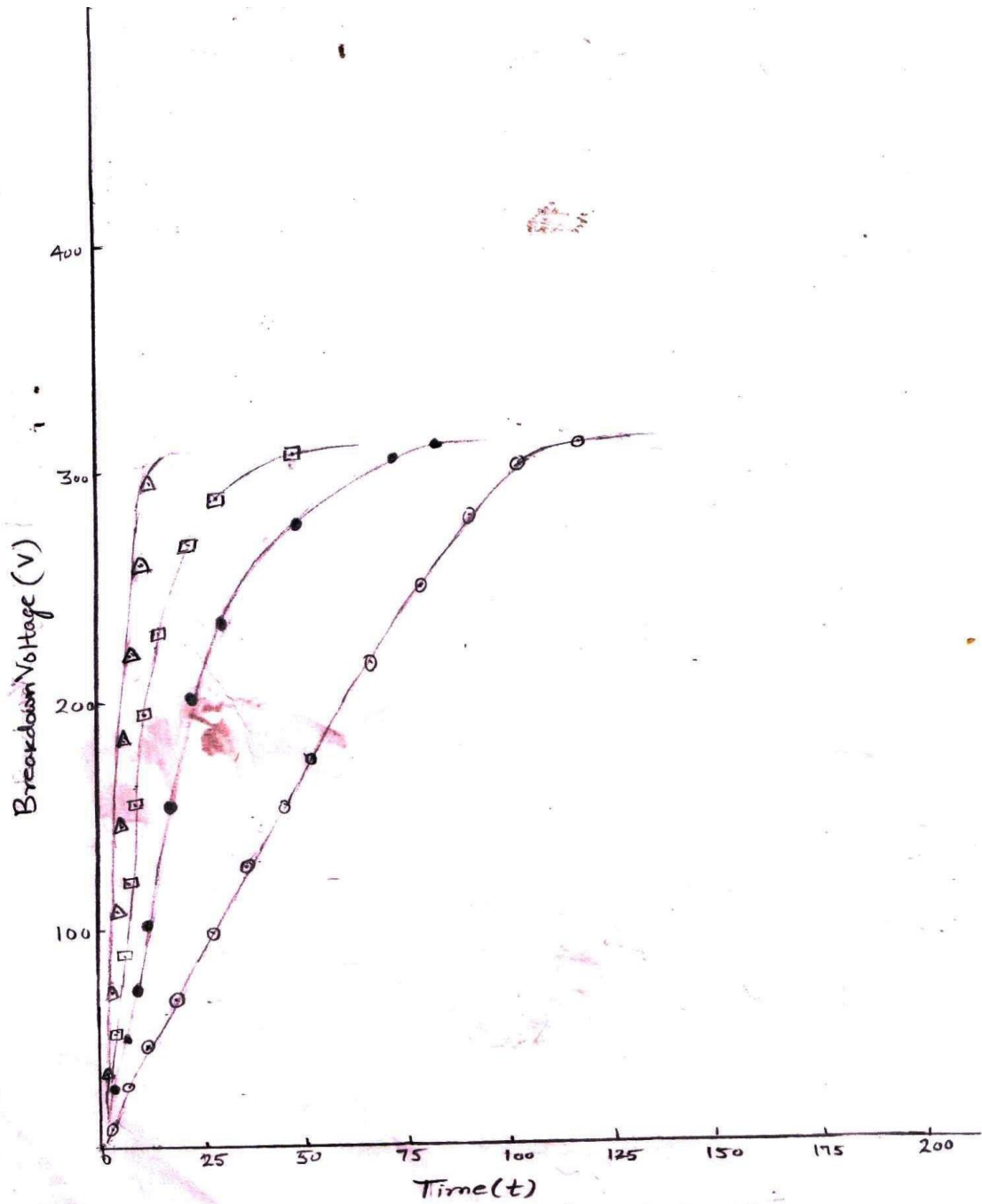
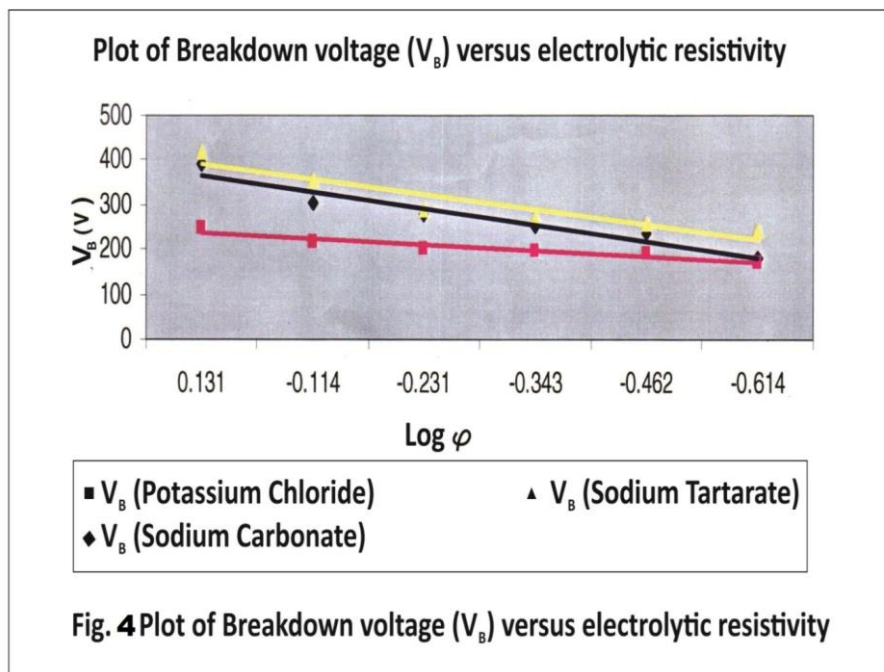
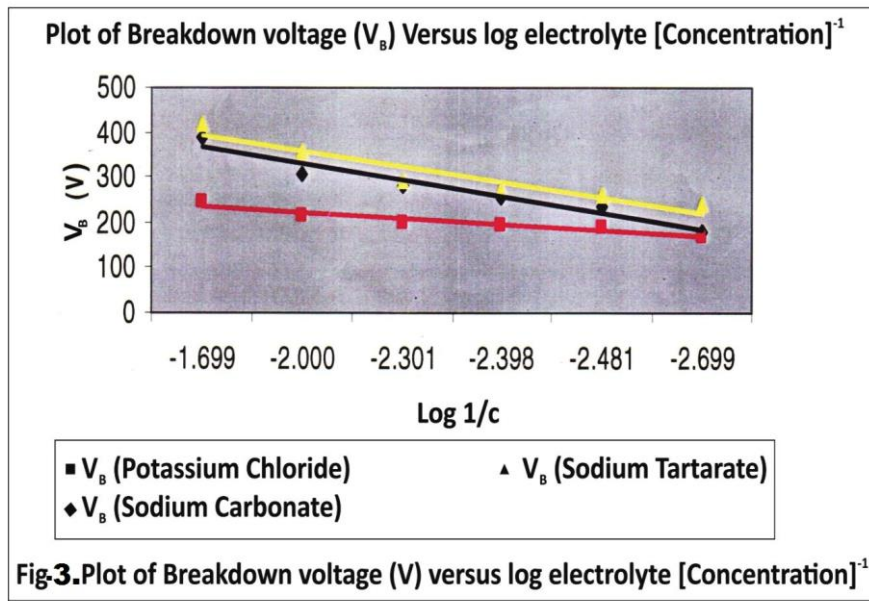


Fig.2. Variation of breakdown voltage with time at different current densities.
[○] 10 A m⁻²; (●) 50 A m⁻²; • 100 A m⁻²; △ 250 A m⁻² □



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