R 366 Philips Res. Repts 14, 123-131, 1959

CURRENT-TIME RELATIONSHIP IN THE FORWARD DIRECTION OF ELECTROLYTIC RECTIFIERS

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Summary

The shape of the forward current as a function of time is given for an electrolytic rectifier, if an alternating rectangular voltage is applied. The loops in the current-voltage characteristic, which occur when a sinusoidal voltage is applied, are explained. It appears that the forward current decreases strongly with increasing blocking voltage. The forward current through the oxide layer hardly depends on the thickness of this layer. A qualitative explanation of the observed phenomena is given.

Résumé

On donne la forme du courant de passage en fonction du temps lorsqu' une tension rectangulaire alternative est appliquée à un redresseur électrolytique. On explique la boucle dans la charactéristique courant-tension dans le cas où une tension sinusoïdale est appliquée. Le courant de passage décroît fortement si la tension dans le sens inverse croît. Le courant de passage dépend peu de l'épaisseur de la couche. Une explication qualitative des phénomènes observés est donnée.

Zusammenfassung

Bei einem elektrolytischen Gleichrichter wurde der beim Anlegen einer rechteckigen Wechselspannung entstehende Vorwärtsstrom als Funktion der Zeit gemessen. Die bei sinusförmiger Wechselspannung in der Stromspannungscharakteristik auftretende Schleife wird erklärt. Es zeigt sich, daß der Vorwärtsstrom bei gleicher Vorwärtsspannung mit wachsender Sperrspannung stark abnimmt. Der Vorwärtsstrom ist nur wenig von der Schichtdicke abhängig. Es wird eine qualitative Erklärung der Erscheinungen gegeben.

1. Introduction

When Al has been covered by electrolytic oxidation with an insulating oxide layer, the system Al-Al_2O_3-electrolyte constitutes a rectifying system. The direction of easy transmission for electrons is from metal to electrolyte. The small current from electrolyte to metal is generally called the leakage current. When a constant direct voltage is applied and the Al forms the negative pole the current is not constant but increases with time [1]).

When an alternating voltage is applied, the *I-V* characteristic shows a loop, in both directions (fig. 1).

We have already mentioned in a prior publication [2]) the fact that, when the Al has been made anode for a relatively long time and the polarity is reversed to that of easy transmission, the current does not attain its constant value immediately but starts with a zero value and gradually increases to an asymptotic

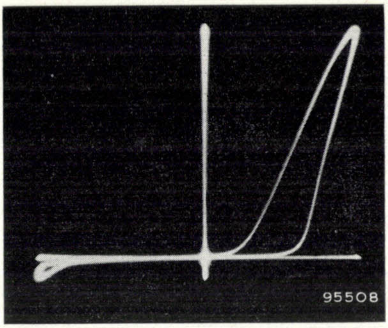

Fig. 1. The current-voltage characteristic when a sinusoidal voltage is applied (200 c/s).

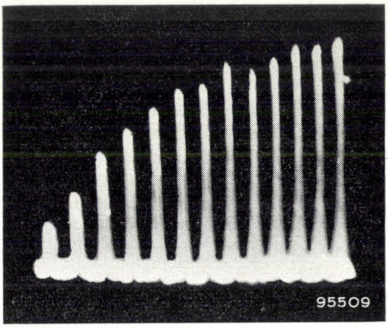

Fig. 2. The current-time characteristic at the initial moment of the application of the alternating voltage, after the Al has been anode for a relatively long time (100 c/s).

value. Figure 2 gives an example of such a current when an alternating voltage has been applied immediately after the Al has been the anode. We observe rectification immediately, whereas the current in the direction of easy transmission increases with each period until it reaches its maximum value.

The purpose of this article is to examine this phenomenon, when a rectangular alternating voltage is applied (fig. 3). From the shape of the current we shall draw conclusions about the loops in fig. 1. We shall also consider the fact that,

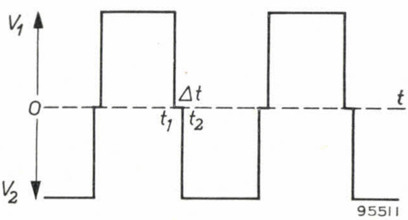

Fig. 3. The shape of the alternating rectangular voltage used.

when an alternating rectangular voltage is applied, the forward current depends strongly on the value of the voltage in the blocking direction but shows little dependence on the thickness of the oxide layer.

2. The experimental apparatus

The rectangular alternating voltage was obtained with an arrangement as shown in fig. 4. Three revolving discs S_1, S_2, S_3 made of insulating material were mounted above one another on a common axis. Copper strips M, which passed under the brushes B, were mounted along the circumference of the discs.

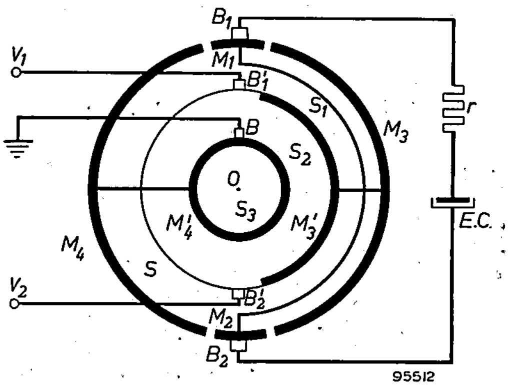

Fig. 4. Equipment used for obtaining a rectangular alternating voltage as shown in fig. 3.

In the position of fig. 4, M_1 is just under B_1, while M_1 is connected to M_2; and the electrolytic system *E.C.*, connected to the brushes B_1 and B_2, is short-circuited. In fig. 3 the short-circuit period lies between the moments t_1 and t_2. When the combination of discs $S_1S_2S_3$ revolves, the metal strip M_3 passes alternately under B_1 and B_2, which are connected with *E.C.* The metal strip M_3' connected with M_3 passes under the brushes B_1' and B_2' which are connected with the poles of the battery. Thus M_3 is alternately connected with these poles. The metal strip M_4, connected with M_4', is via brush B connected to earth. We obtain in this way an alternating voltage, separated by periods of short-circuiting. This short-circuiting is effected so that capacitive charges may flow away. We substituted a normal condenser of the same capacitance in the place of our electrolytic system in order to check whether troublesome charges and discharges were caused by the rather large capacitance of our system. This might have influenced our results, but it was found not to be the case. The current passing through the electrolytic system in fig. 4 gives rise to a voltage across the resistance r, which is applied to an oscilloscope; the image on this oscilloscope is photographed. When necessary we corrected for the voltage drop across the electrolyte and r. We also see that it is possible to vary the voltages.

We generally used Al plates covered with an oxide layer 0·1 μ thick and with a surface of 2 cm^2 the capacitance of which was about 0·1 μF. The Al was of a purity of about 99·98 %; we used an aqueous solution of boric acid and borax. All experiments were carried out at room temperature.

3. Experiments

(a) *The current in the forward direction as a function of time*. First of all we applied a rectangular alternating voltage as indicated in fig. 3. The voltages in the two directions were of the same amplitude. The current in the forward direction as a function of time is shown in fig. 5, and from this follows approximately the relationship: $I = I_m (1 - e^{-kt})$. It must be emphasized that this curve

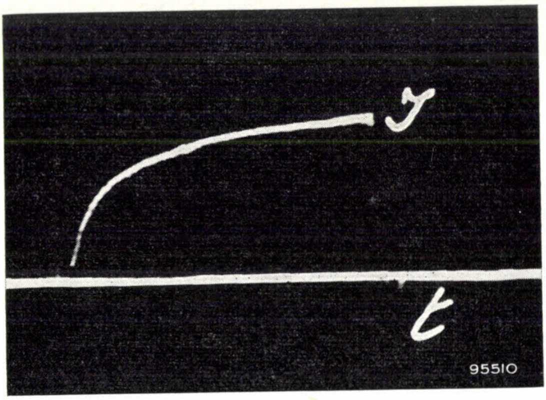

Fig. 5. The build-up of the forward current as a function of the time when a tension as shown in fig. 3 was applied. The curve is described in 0·06 sec.

was measured some minutes after the rectangular alternating voltage had been applied. If we apply the rectangular alternating voltage immediately after the Al has been the anode for a relatively long time, the saturation value i_m reached in each half period can be written as a function of the number n of periods passed: $i_m = I_m(1 - e^{-k_1 n})$, where k_1 is a constant. The saturation value increases till a maximum is reached. Figure 6 shows the current in the forward direction at varying times (*a* to *d*), immediately after the rectangular alternating voltage had been applied, the Al having been the anode for a relatively long time. Figure 6 is in fact a repetition of fig. 2. Rectification is present from the beginning, whereas the saturation value of the current builds itself up till a maximum has been reached and this is the situation as shown in fig. 5.

(b) *The saturation value of the forward current as a function of the voltage in the blocking direction*. It was found during the measurements that the value of the saturation value I_m of the forward current was a function of the value of the voltage in the blocking direction.

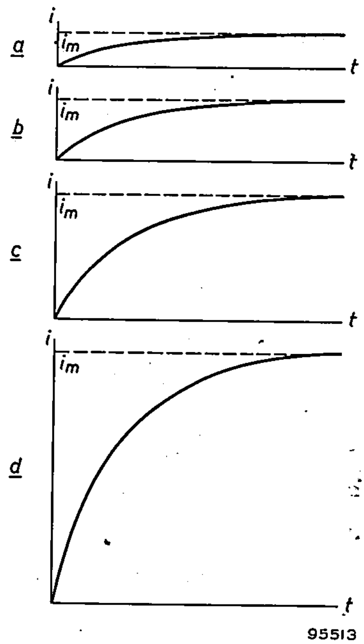

Fig. 6. The forward current as a function of the time when alternating rectangular voltage is applied, at different moments (*a, b, c, d*) after the Al has been anode for a relatively long time.

Figure 7 gives the saturation value I_m of the forward current, when a voltage of 8·3 V was applied, as a function of the voltage in the blocking direction. At a blocking voltage of about 14 V the current in the forward direction has only a very small value. This proves that we cannot speak of a value of the forward current without taking into account the voltage in the blocking direction. In fig. 8 the logarithm of the saturation value of the forward current has been plotted against the blocking voltage. We see that we may write:

$$I_m = a \exp(-bV_s),$$

where I_m is the forward current, V_S the blocking voltage, while a and b are constants.

(c) *The dependence on the forward current upon the thickness of the layer.* An alternating rectangular voltage of 12 V was applied to oxide layers of varying thicknesses and the saturation value of the current was measured. The result is shown in fig. 9. The value of the current did not change more than 20% for a variation in the thickness of the layer from $2{\cdot}6.10^{-6}$ cm to $1{\cdot}6.10^{-5}$ cm. The voltages in the two directions had the same amplitude.

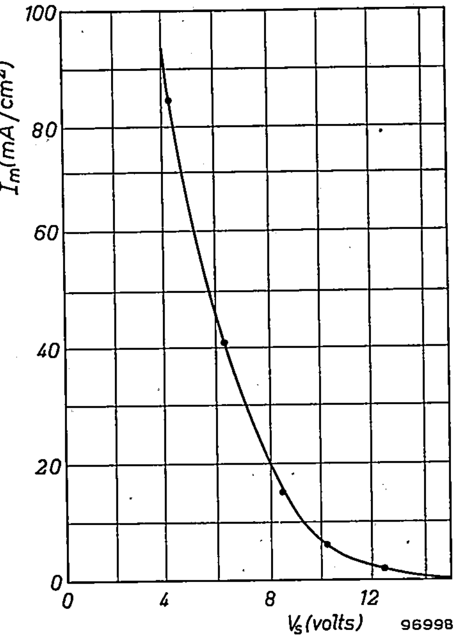

Fig. 7. The forward current as a function of the reverse voltage.

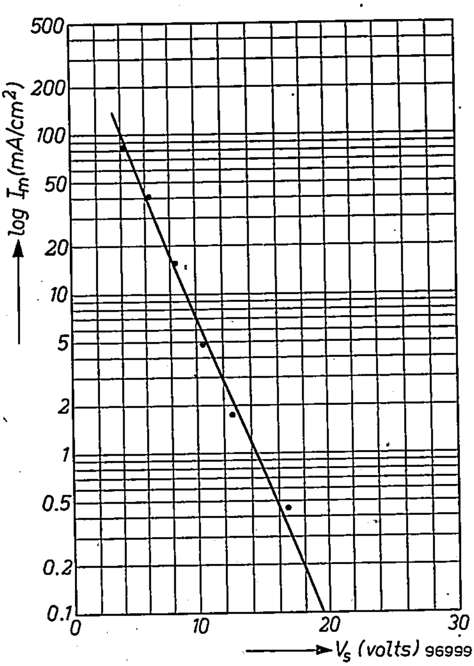

Fig. 8. The logarithm of the forward current is plotted against the reverse voltage.

The same result was obtained with alternating sinusoidal voltages. To pass a current of 3·5 mA/cm² through a layer of 5.10⁻⁶ cm, an alternating voltage of 7 V was necessary.

For a layer about 6 times as thick, a voltage of 9·5 V had to be applied, which is only 30% higher. So it appears that the relation between the current and the applied voltage depends only little on the thickness of the layer.

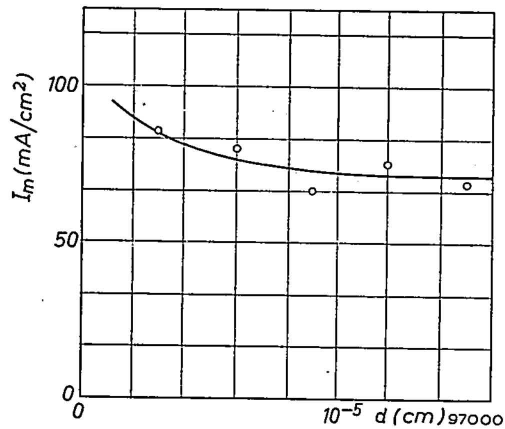

Fig. 9. The saturation value of the forward current when a rectangular voltage is applied, as a function of the thickness of the layer.

4. Conclusions

First of all we shall consider the loop in the *I-V* characteristic. In every half period of the alternating sinusoidal voltage there are two values of t for which the voltage has the same value. But as shown in fig. 5, at least in the part of the curve where the saturation values have not yet been reached, the current I has different values for these two values of time, the value of I for the greater t being larger than for the smaller one. This means that the *I-V* characteristic shows a loop. The fact that the loop also appears in the leakage current means that the *I-t* curve for the leakage current has the same shape as that shown in fig. 5. The character of these *I-t* curves is shown again in fig. 10. In fig. 1 both loops are described in an anti-clockwise direction. It is difficult to explain the shape of the *I-t* curves of figs 5 and 6. The difficulty is caused by the fact that there are ionic and electronic currents at the same time. We know that when a voltage is applied in the forward direction a deformation of the layer takes place. This means that ions have been displaced [3]. The assumption can be made that in this case Al^{+++} ions are displaced towards the Al, which is the negative pole, and a space charge is formed. The residual voltages occurring prove that such a displacement has happened [4]. We assume that the potential distribution at the side of the Al is as given in fig. 11. Here electrons can pass the potential barrier by cold emission.

It might be possible that the width of this potential barrier will not depend greatly upon the thickness of the oxide layer, which would explain qualitatively the fact that the current is almost independent of the thickness of the layer.

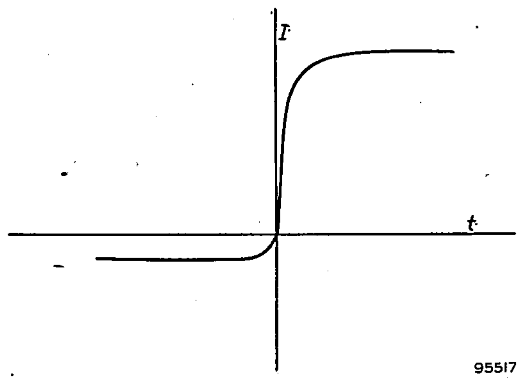

Fig. 10. The shape of the current in both directions when a rectangular alternating voltage is applied.

We can also explain the results shown in fig. 6 in a similar way. Initially the potential barrier as shown in fig. 11 has a width nearly equal to the thickness of the oxide layer, but this gradually decreases when the ions start accumulating at the oxide-aluminium interface. At the same time more and more electrons can pass the potential barrier by cold emission.

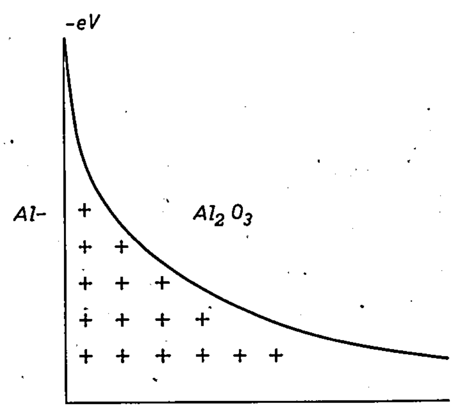

Fig. 11. The potential curve inside the layer at the side of the Al after the Al has been the negative pole for some time.

The building-up of the barrier takes a few minutes. Diffusion causes a drift of aluminium ions in the opposite direction and an equilibrium condition will be established. The current in this situation is represented in fig. 5. As soon as a reverse potential is supplied, Al^{+++} ions are driven away from the Al oxide interface to the oxide and at the next reversal of the potential (Al—) the barrier has to be brought to its former shape, so that electrons can pass again.

In this way we see that for higher reverse voltages it is more difficult to build up a potential barrier with smaller width, so that less electrons can pass through the barrier.

The authors are well aware of the fact that their discussion is only a qualitative one. They wish to thank Mr B. C. Bouma, who performed the first experiment showing an *I-t* dependency in the forward direction. They are indebted to Dr P. Winkel for discussions on the subject.

Eindhoven, October 1957

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