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Instructions for use

The Electrolytic Aluminum-Oxide Rectifier

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The rectifying property of electrolytic Aluminum-Oxide is obliged to a double layer made between negative ions, which are adsorbed on oxide film in electrolytic solution, and positive charges induced in metal by them. A relation of electric resistance with applied voltage is obtained, and it is shown that current carriers in Al_2O_3 are Al^+ ions and the film of Al_2O_3 is about 10^{-5} cm in thickness.

I. Introduction

It is well known that certain metals, notably aluminum and tantalum, as anode in a suitable electrolyte become coated with a thin oxide film, and then exhibit rectifying properties: the currents are very small for the aluminum positively charged with respect to the solution, while for opposite polarity they may be very large.

According to MIYAZAWA[1] the process of formating an oxide film is caused by Al ions flowing from the aluminum through the oxide into the solution under the influence of the high electric field in the layer and combining with oxygen ions, the thickness of the oxide film increases. For constant applied voltage the current decreases exponentially with time until a small current of less than a microampere per cm² remaines flowing, so that after several hours remarkable increase of the thickness cannot be measured. The thickness of the layer is proportional to the formation voltage and of the order of 10^{-5} cm—10^{-6} cm. The purpose of this paper is to discuss the mechanism of the electric conductivity of the aluminum rectifier.

II. The Experimental Data

The oxide film is formed on an aluminum plate in a solution of borax (4gr/200cc) and a carbon electrode is used as cathode.

The representative relationship between applied voltage (below the formation voltage and resistance per cm² of the film on an aluminum anode is shown in Fig. 1. The exact values of resistance are somewhat unstable, especially in low voltages. But the most stable curves of which we obtained are shown. In Fig. 1 the resistance-voltage curves I, II, III are corresponding to the specimens of formation voltages of 95 volt/one hour, 49 volt/one hour and 24.5 volt/3 hours.

From these curves the maximum resistances are 42MΩ, 30MΩ and 16MΩ and the corresponding applied voltages are 1.6 volt, 1.25 volt and 1.0 volt respectively. The coated surface is seen to be coloured and the thickness l of the film is estimated from the capacity C, by setting

$$l = \kappa/4\pi C , \tag{1}$$

where κ is the dielectric constant, which we may take to be of the order of 10. For the specimens I, II, and III in Fig. 1 the capacities are 0.0656 $\mu f/cm^2$, 0.125 $\mu f/cm^2$ and 0.197 $\mu f/cm^2$ and, therefore, their thickness are estimated as 1.31×10^{-5} cm, 0.705×10^{-5}cm and 0.502×10^{-5} cm.

III.   Mechanism of the Electric Conductivity

It is shown that the application of a positive potential to the aluminum results in a high resistance, whereas the application of negative potential results only in very low resistance. The rectification may be based on the oxide layer and the negative ions which are adsorbed on the surface of the layer.

If we assume that the electrons carry the current moving through the uniform Al_2O_3 layer, and the rectifying action is occured between Al_2O_3 oxide layer, and the Al metal, so the aluminum must be negative in the blocking direction, because Al_2O_3 is the N-type semi-conductor. If we assume the other case in which the current carrier is electron and the rectification takes place at the contact of Al_2O_3 and the negative ions on the surface of Al_2O_3, so the electrons escape from the negative ions and oxygen gas should be produced. But, in practice, we can see only a stream of very minute gas bubbles on the anode. If the above mentioned assumption is correct the amount of oxygen gas must be the half

of the hydrogen gas , so we cannot assume that the current carrier is the electron in the blocking direction.
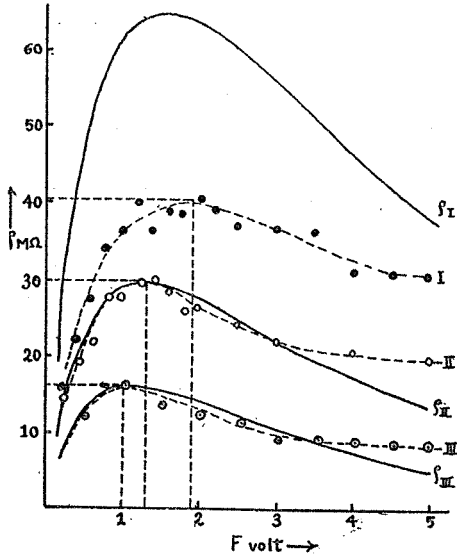

Fig. 1.

For the previous reason, it is supposed that the Al ions carry the current and at the same time form the oxide layer. When the thickness of the layer reaches the value of the order of 10^{-5} cm, the rate of growth becomes negligible small. The Al ions seem to move through the oxide under the influence of an electric double layer, which is formed by the negative ions in contact with Al_2O_3 and the induced positive charge on the surface of the aluminum. In view of this model MOTT's theory of rectifier is applicable.[2]

Let v be the mobility and D the diffusion coefficient of an aluminum ion. Let x denote distance measured from the metal surface into the oxide layer, and let $n(x)$ be the density of the stoichiometric excess aluminum ions. Then the current j per square centimeter in the oxide layer under the influence of the electric field strength F' is given by

$$j = n(x)evF' - De(dn/dx) , \qquad (2)$$

where e is the electric charge of an aluminum ion. Integrating this equation for n, and making use of the Einstein equation

$$v/e = D/kT \qquad (3)$$

we obtain

$$n(x) = j/evF' + A \exp(eF'x/kT) , \qquad (4)$$

where A is a constant. At $x = 0$ and $x = l$ the value of $n(x)$ becomes

$$n(0) = j/evF' + A \qquad (5)$$

and

$$n(l) = j/evF' + A \exp(eF'l/kT). \tag{6}$$

Under these boundary conditions the current j can be written as

$$j = \frac{evF'\{n(0)\exp(eF'l/kT) - n(l)\}}{\exp(eF'l/kT) - 1}. \tag{7}$$

F' can be separated into two parts; one is external voltage F and the other induced voltage F_0 by the presence of negative ions on the surface of Al_2O_3. F_0 is determined by the density of negative ions and increases somewhat with increasing the current, but it will be nearly constant to changes of barrier thickness if the same electrolyte electrode are used. Therefore F' and j are

$$F' = F + F_0 \tag{8}$$

and

$$j = \frac{ev(F_0 + F')[n(0)\exp\{e(F_0 + F')l/kT\} - n(l)]}{\exp\{e(F_0 + F')l/kT\} - 1}. \tag{9}$$

In the absence of an external field, the current becomes zero, so

$$n(l) = n(0)\exp(eF_0l/kT) \tag{10}$$

and

$$j = \frac{ev(F_0 + F')\,n(0)\exp(eF_0l/kT)\{\exp eFl/kT) - 1\}}{\exp\{e(F_0 + F')l/kT\} - 1}. \tag{11}$$

Under the condition $e(F_0 + F')l/kT$ at room temperature the equation (11) can be written as

$$j = ev(F_0 + F')\,n(0)\{1 - \exp(-eFl/kT)\}. \tag{12}$$

If we consider the image force by the aluminum metal, the height of the potential barrier which the Al ions must overcome from the Aluminum to the oxide layer, reduced by

$$e^{\frac{3}{2}}F'^{\frac{1}{2}}\kappa^{-\frac{1}{2}} = e^{\frac{3}{2}}(F_0 + F)^{\frac{1}{2}}\kappa^{-\frac{1}{2}} \tag{13}$$

Thus n_0 in the equation (12) should be replaced by $n(0)\exp\{e^{\frac{3}{2}}(F_0 + F)^{\frac{1}{2}}/\kappa^{\frac{1}{2}}kT\}$, and the expression for the current becomes

$$j = ev(F_0 + F')n(0)\exp\{e^{\frac{3}{2}}(F_0 + F)^{\frac{1}{2}}/\kappa^{\frac{1}{2}}kT\}\{1 - \exp(-eFl/kT)\} \tag{14}$$

and resistance

$$\rho = \frac{1}{ev\,n(0)}\,\frac{F}{F_0 + F}\,\frac{\exp\{-e^{\frac{3}{2}}(F_0+F)^{\frac{1}{2}}/\kappa^{\frac{1}{2}}kT\}}{1-\exp(-eFl/kT)}\,, \qquad (15)$$

where Fl is great compared with 0.1 volt. So it is

$$\exp(-eFl/kT) \ll 1\,,$$

and

$$\rho = \frac{1}{evn(0)}\,\frac{F}{F_0 + F}\exp\{-e^{\frac{3}{2}}(F_0+F)^{\frac{1}{2}}/\kappa^{\frac{1}{2}}kTl^{\frac{1}{2}}\}\,. \qquad (16)$$

In this equation F and F_0 per unit length are replaced by the actual terminal voltage of the layer.

In our experiment the specimen II showed the most stable results, so that we compared the formula (16) with the curve II in Fig. 1 and determined the $n(0)$ and F.

In the equation (16) e is the charge of an aluminum ion, but when the stoichiometric excess Al^{+++} are present, there will be a tendency that the Al^{+++} ion attracts more electrons around it and becomes probably Al^+ or Al^{++}. If, therefore, Al^+ is the current carrier, e equals e', i.e. $e' = 4.8 \times 10^{-10}$ c.g.s. e.s.u.. The mobility of Al ion, $v = v_0\exp(-U/kT)$, is about 1.7×10^{-8} cm/sec-volt at the temperature of 291°K, when we adopt in ionic crystal the usual values of v_0, which is 0.5 cm/sec, and U 10,000 cal/mol.

F_0 and $n(0)$ are determined by making the equation (16) in agreement with the experimental curve of the specimen II at its maximum value. The maximum resistance of the specimen II is $30 \times 10^6 \Omega/cm^2$ at $F = 1.25$ volt, so

$$F_0 = 2.04 \text{ volt} \qquad\qquad\qquad (17)$$

and $\quad n(0) = 1.83 \times 10^{18}/cm^3$. $\qquad\qquad (18)$

N is estimated to be of the order of $1.1 \times 10^{11}/cm^2$ from the equation

$$F_0/l = 4\pi e\,N\,, \qquad\qquad\qquad (19)$$

where N is the number of ions absorbed on Al_2O_3 surface. The number of excess Al ions on the contact surface between Al and Al_2O_3 can be determined by the energy required to remove an Al ion from Al to Al_2O_3, but it cannot be obtained exactly. Assumed now $e = 2e'$, i.e. Al^{++} are the current carrier, $n(o)$ becomes roughly $10^{11}/cm^3$; this seems too small. Accordingly we must assume that

the conductivity is caused by Al$^+$ ions.

Introducing the values of (17) and (18) into the equation (16), so it is

$$\rho_{\text{II}} = 2.01 \times 10^9 (F/F + 2.04) \exp\{-1.79 (F + 2.04)^{\frac{1}{2}}\} \ \Omega/\text{cm}. \quad (19)$$

This is shown in Fig. 1. In the case of the specimen I and III the capacity is $0.0656 \ \mu f/\text{cm}$ and $0.197 \ \mu f/\text{cm}$ and hence the thickness is 1.31×10^{-5} cm and 0.0502×10^{-5} cm. F_0 and $n(o)$ are used in this case also the same value of specimen II, because they may be independent on the changes of the barrier thickness as obviously mentioned if the same electrolyte and electrode are used. We obtain

$$\rho_{\text{II}} = 2.01 \times 10^9 (F/F + 2.04) \exp\{-1.37 (F + 2.04)^{\frac{1}{2}}\} \ \Omega/\text{cm}, \quad (20)$$

and

$$\rho_{\text{III}} = 2.01 \times 10^9 (F/F + 2.04) \exp\{-2.13 (F + 2.04)^{\frac{1}{2}}\} \ \Omega/\text{cm}. \quad (21)$$

ρ_{I} and ρ_{III} are represented in Fig. 1. The reasons for the discrepancy between the theoretical and experimental values are probably that (1) the thickness of the layer is not obtained exactly, (2) F_0 is not constant in practice, (3) the electronic current is neglected. Especially the electronic current from negative ions increases with increasing the applied voltages, so that the experimentally obtained resistance is lower than the theoretical value.

Let ρ_{I} coincide with the observed ρ, the thickness becomes 0.9×10^{-5} cm for the same value of $n(o)$ and F_0, and this is a reasonable value.

Fig. 2.

The relation between the thickness of the oxide layer l and F_M, at which the resistance exhibits the maximum value, is obtained from the equation (16)
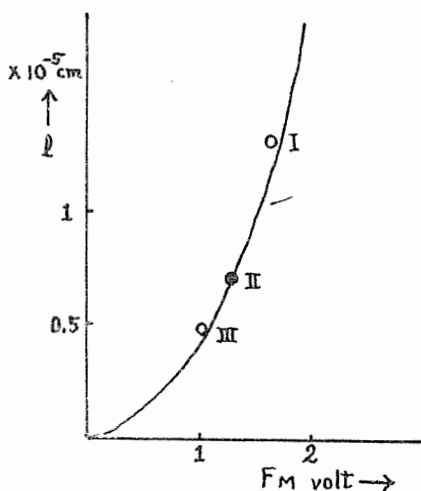
$$l = (e^{\frac{3}{2}}/2\kappa^{\frac{1}{2}}kTF_0)^2 F_M^2 (F_M + F_0) . \tag{22}$$

Applying again $F_0 = 2.04$ volt, it is obtained for l

$$l = 0.137 \times (2.04 + F_M) F_M^2 . \tag{23}$$

Fig. 2. represents a good agreement with experimental results.

References

(1) H. MIYAZAWA, S. NISHIKAWA and H. MORIKAWA: *Toshiba-Review*, **3** (1949), 4 (in Japanese).

(2) N. F. MOTT: *Proc. Roy. Soc.* (A), **171** (1939), 27.

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