ON THE THEORY OF THE ELECTROLYTIC RECTIFIER.[1]

By K. E. Guthe.

A POLARIZED electrolytic cell put in an alternating current circuit will always produce a shifting of phase since the current must necessarily become zero when the impressed E.M.F. at the electrodes equals the counter E.M.F. of polarization. The current will lead in phase or, with other words, the electrolytic cell produces the same effect as an electrostatic condenser and we speak therefore of an electrolytic capacity, without however attributing the condenser effects in the two cases to the same cause.

If the counter E.M.F. of polarization on one electrode obtains very different values according to the direction of the current through the cell, then for a given alternating impressed E.M.F. more current will flow in one direction than in the other, or we have what is called an "electrolytic rectifier." A well-known cell, showing this property in a marked degree is the aluminium rectifier, consisting of an aluminium and a carbon (or platinum) electrode, immersed in a solution of a salt of a rather complicated chemical structure, usually alum, $KAl(SO_4)_2$. This cell allows only a very small current to pass from the aluminium to the carbon, while the current in the opposite direction is not obstructed.

To explain this phenomenon two different points of view may be chosen. Either we may consider the obstacle to the current, when the aluminium forms the anode, as a very high ohmic resistance between the liquid and the plate. In fact, a badly conducting whitish film of some oxide or hydroxide of aluminium covers the "formed" plate.

Or we may explain the effect as being due to polarization with a very high counter E.M.F., produced only when the aluminium forms the anode, while it has a value not higher than usual with the

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[1] Paper read before the Pittsburg meeting of the A. A. A. S.

current flowing in the opposite direction. On Fig. 1 two curves are plotted showing the relation between the terminal potential difference and the current: curve I., when the aluminium is the anode, curve II., when it is the kathode.

The curves closely resemble those obtained by Le Blanc and others for ordinary polarization, except that the point where curve I. bends around corresponds to about thirty volts instead of one or two volts. If we take the point of view first mentioned, we must assume the resistance to be a variable quantity decreasing with an increase of current, *i. e.*, we have to deal with something quite analogous to the "resistance of transition," formerly so often met with in the discussion of ordinary cells. In a former paper[1] I have shown that, at least in the case of copper in copper sulfate solution, polarization will sufficiently account for this apparent, variable resistance.

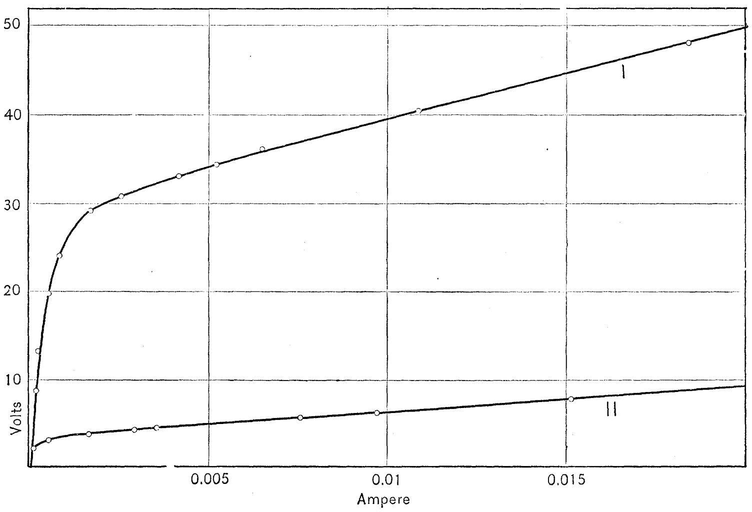

Fig. 1.

I prefer, therefore, to look at the problem from the second point of view and state it in the following way: By some cause, whatever it may be, most of the negative ions are prevented from reaching the anode as long as the terminal potential difference remains below

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[1] PHYS. REV., 7, p. 193, 1898.

a certain high value, while the kations are not affected more than is the case in ordinary polarization. What is the cause for this?

So far every one experimenting with the aluminium rectifier assumes it to be the layer of oxide, mentioned above. But this seems to me rather improbable. In the case the aluminium forms the anode, we must suppose that with increasing current the layer breaks down or that holes appear in it which close up again, as soon as the current is decreased. We should then expect quite irregular results, but in fact the resistance returns with remarkable regularity to the same value for the same current, no matter whether the current before was larger or smaller. Besides, this return takes place very rapidly, while the changes in resistance are quite slow during the original formation of the film. This contradiction becomes most apparent, when the current is first sent towards the aluminium. The plate acts practically as if no additional resistance besides the electrolytic were present. The oxide film should then be broken up entirely. But as soon as the current is reversed the high resistance forms within a few minutes. Why should the holes close up almost instantly when the formation of the high resistance on a clean plate requires a considerable time? An inspection of the film shows, moreover, that in spite of the various changes of the current it seems to remain unchanged.

If we suppose that the film in question is not the solid oxide film, but of a fluid nature which gives way if the strain becomes too large, but otherwise remains in its position, all the above objections are removed. In order to show that there is such a film on the electrode, I put a cell in which a high resistance aluminium plate was previously formed under the receiver of an air-pump and, when the pressure was sufficiently reduced, could see a stream of very minute gas bubbles escape from the electrode. After this the resistance was quite low, but increased rapidly to its original value as soon as a current was sent through the cell with the aluminium as the anode. When standing for some time, especially after having been in a vacuum, the plate shows a very low resistance, because the gaseous film has been dissolved in the electrolyte.

A point of practical interest is, that after a plate has stood for some time in the solution the film seems to disappear at the surface line of the liquid, thus lowering the resistance. To get consistent results I had always to raise the plate one or two millimeters before taking a series of observations.

The first result of this investigation is, therefore, that *the high resistance in the aluminium rectifier is due to a thin film of gas, probably oxygen,* which prevents the passage of the negative ions from the solution to the electrode. Only in places where an accidental concentration of energy occurs, the strain may become too great and some ions may break through. This would explain the small current, present even with a low potential difference at the electrodes, the "Reststrom" as it is called in German. If we bring a wire into the liquid and hold it near the electrode, sparks will cross from one to the other and the current increase, to drop again to its low value as soon as the wire is removed.

This theory will also explain the passage of a large current in the direction from the carbon or platinum to the aluminium electrode. Now hydrogen is set free at the latter, but the hydrogen gas is able to escape through the fine meshes of the oxide film in which the oxygen gets so hopelessly entangled. Gas is developed freely at the electrode and there is no high resistance in this case.

One serious objection against the supposition that the resistance is formed by a solid film broken in various places by the current, lies in the fact, that the current hardly changes when we diminish the size of the plate to a very small fraction of the original. Polarization on the other hand would lead us to expect this result.

The following conclusions were drawn from the foregoing considerations and verified by experiment:

1. An increase in temperature will increase the current. The energy of the ions will increase and for a given potential difference, more of them will pass through the gas film. The curves on Fig. 2 show this to be the case. They represent only the observations with the aluminium as anode.

2. The concentration of the electrolyte should have no influence upon the phenomenon. I varied the concentration within wide limits without observing any change in the resistance of the film.

3. The results should not differ appreciably with different electrolytes, as long as similar reactions take place at the anode. I took

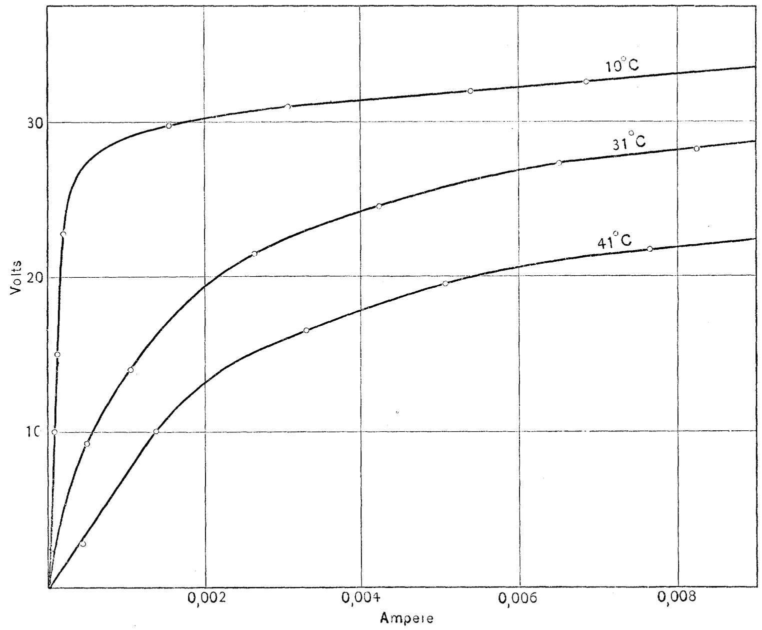

Fig. 2.

two sets of observations, one with solutions of alum (1), ferrocyanide of potassium (2), and zinc sulfate (3) and another with solutions of alum (1′), Rochelle's salt (4) and coppersulfate (5).

The curves are given on Fig. 3 and show that all agree as well with each other as successive tests with the same plate in the same electrolyte would do.

4. The plate may behave quite differently towards other negative ions. A plate showing a high resistance in alum solution offered no resistance when immersed in sodium chloride solution. The chlorine acts as the hydrogen in this respect.

We have then a kind of a semipermeable membrane, which allows certain ions to pass through it and give off their electrical charges at the electrode, while it prevents the passage of other kinds of ions.

It seemed of sufficient interest to study the action of the well-known semipermeable membrane of copper ferrocyanide in this respect. Dr. G. A. Hulett kindly prepared one for me, forming it in a porous cup. The results correspond closely to those obtained

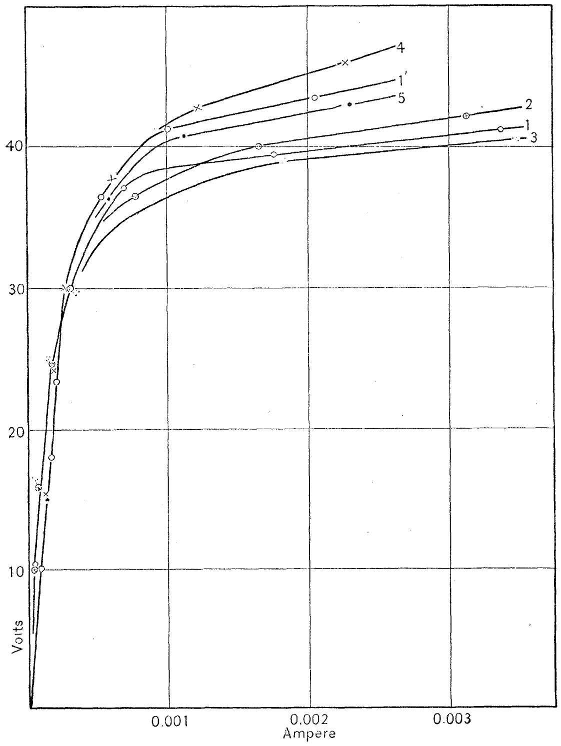

Fig. 3.

with the aluminium cell. Inside the cup was placed a copper electrode immersed in copper sulfate solution, outside a platinum electrode in a solution of potassium ferrocyanide. A high resistance seemed to be present when the current passed from the copper to the platinum, hardly any with the current in the opposite direction. Curves *a* and *a'*, on Fig. 4, show the results obtained with such a cell.

Of course, it does not follow, that the process in this semipermeable membrane is necessarily identical with the one assumed for the aluminium plate covered with an oxide film. Gases seemed, however, to be developed at the porous cup when the current flowed towards the platinum. A further investigation of this subject would be of great interest.

The copper ferrocyanide membrane was also formed by immersing the copper plate directly in the cyanide solution. In this case the hydrogen gas developed between membrane and plate, breaking the membrane off after having collected in sufficient quantity. Otherwise the phenomenon resembles closely that shown by an aluminium electrode. Curves *b* and *b′*, of Fig. 4, were obtained with such a plate.

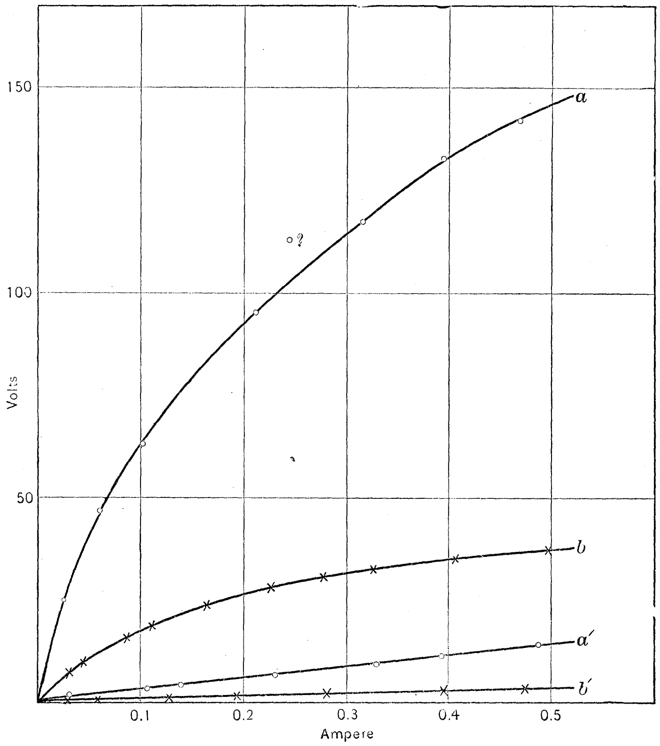

Fig. 4.

The fact, that the polarization falls off very rapidly in the aluminium cell, has been brought forward against the polarization theory. But the polarization is in this case due to the accumulation of ions in the solution only and will, therefore, disappear very rapidly. In ordinary electrolytic polarization there is in addition an occlusion of the ions in the metal of the electrode and this is the cause for the slowness with which it disappears.

In conclusion, we may ask if it may not be possible to explain ordinary polarization as being due to a very thin, non-conducting fluid membrane—possibly pure water as the outermost layer of any solution—which has first to be broken through before the ion reaches the metal. The differences in the value of hydrogen polarization, according as it is developed on platinum, lead or mercury surfaces seem to point to an important influence of the action between the surfaces of the metal and the electrolyte.

Physical Laboratory of the University of Michigan,
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