HIBRID PARAMETERS OF AN ELECTROLYTIC ACTIVE TWO-PORT*

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The electrolytic active two-port, i.e. the electrolytic analogue transistor, is an operating model of the junction transistor. A base electrode is a low-resistance contact with the solution and also serves to maintain the ratio of oxidized and reduced ions at an equilibrium value, thus establishing the potential of the solution. The collector electrode is placed within a few tenths of millimeter to the emitter, and so biased that the minority ions (the oxidized ones) diffuse from the emitter to the collector surface where they will be reduced. In the very low frequency band the device has similar parameters — as those of the junction transistor as it will be seen on the recorded Nyquist diagram.

It is possible to make an electrolytic two-port cell which is analogous to the junction transistor. If the solution in the cell is reduced, the model is PNP, if the solution is oxidized the model is NPN.

The base electrode maintains the potential of the solution. It means that the base electrode has to be poorly polarizable (calomel) which interacts reversibly with one or more of the ionic species in the solution. The emitter and collector are highly polarizable electrodes (Pt) such that little current flows unless the voltage difference between one of the electrodes (the emitter) and base exceeds a critical value (the decomposition potential) for oxidation to

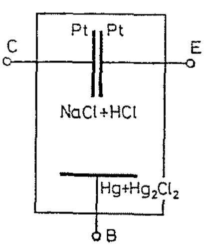

Fig. 1

* Abridged text of the Doctor's Thesis by the author. 1974.

occur. Ions oxidized at the emitter, diffuse to the collector where the reverse reaction occurs by the return of the ions to the reduced state. If the polarity of the electrodes is opposite the reduction will occur at the emitter (PNP, NPN).

The conductivity of the applied solution (1M NaCl and 0.2M HCl) is high enough to keep the electric field and consequently the potential difference in the body of the electrolyte very low. The flow of ions mainly occurs by diffusion.

Theory of the electrochemical cell

The cell is schematized in Fig. 1. The potential of the collector will be determined by equilibrium

$$2Cl^- - 2e^- = Cl_2 \quad \text{(oxidation)} ; \tag{1}$$

that of the emitter:

$$Cl_2 + 2e^- = 2Cl^- \quad \text{(reduction)} . \tag{2}$$

Let us assume a Cl_2 concentration at the collector c_2 and at the emitter zero; and a Cl^- concentration of c_1 and c_3 at the collector and the emitter, respectively.

The current density can be expressed as

$$i = \frac{2eD_2c_2}{l} = \frac{eD_1(c_3 - c_1)}{l} \tag{3}$$

where D_1 and D_2 are diffusion coefficients for Cl^- and Cl_2, respectively,
l is the emitter to collector spacing.

Assuming the total concentration to be constant, we have

$$2 \frac{1}{2} c_2 + \frac{1}{2} (c_1 + c_3) = c_{10} \tag{4}$$

where c_{10} is the equilibrium concentration of the Cl^- ions.

The equilibrium concentration of Cl_2 is determined by

$$Hg + \frac{1}{2} Cl_2 \rightleftarrows \frac{1}{2} Hg_2Cl_2. \tag{5}$$

The current determined by the diffusion is expressed by the following equation:

$$\frac{c_2}{c_1} = \frac{c_{20}}{c_{10}} \exp \left(\frac{ZF}{RT} \Delta\varepsilon \right) . \tag{6}$$

Eqs (3), (4) snd (6) must then be solved for concentration and current density. One is led to a quadratic equation for c_1 whose explicit solution, will not be given. When $\Delta\varepsilon$ is very large, the current tends to a saturation constant value. When $\Delta\varepsilon$ is small, c_1 is nearly equal to the equilibrium value between c_{10} and c_2 (and thus i) varies according to exp $(ZF/RT)\ \Delta\varepsilon$.

Further relationships are required to determine the characteristics of electrolytic cell. The current density value versus $\Delta\varepsilon$ between the collector and emitter electrodes can be expressed as

$$\Delta\varepsilon = \frac{RT}{ZF} \ln \left(1 - \frac{i_d}{i_{d,h}}\right) \tag{7}$$

because the collector electrode is polarizable. From (7)

$$i_d = i_{d,h}\left(1 - e^{-\frac{ZF}{RT}\Delta\varepsilon}\right) \tag{8}$$

where the current density limit of diffusion is

$$i_{d,h} = \frac{eDc_3}{l} \tag{9}$$

thus

$$i_d = \frac{eDc_3}{l}\left(1 - e^{-\frac{ZF}{RT}\Delta\varepsilon}\right). \tag{10}$$

The c_3 value on the emitter in Eq. (10) will be determined by the base current because of the polarization of the collector. Increasing the base current the value of $i_{d,h}$ also will be increasing, corresponding to the set of characters of the electrolytic transistor.

1. The design of the cell

The cell has been constructed for the experimental demonstration of the theory. It has two Pt electrodes as discs (10 mm diameter) for collector and emitter, and a calomel-covered mercury pool for base. The spacing of the Pt disc electrodes may be controlled by a 0.1 mm thick styroflex foil. The cell is constructed from polymetacrylate glass known to be a good electric insulator. The electrical leads are insulated from the solution by being inserted through the cell framework. The electrolytic solution is 1M NaCl and 0.2M HCl.

2. Static characteristics of the cell

The scheme of the cell is shown in Fig. 2. E, C, B are emitter, collector and base, respectively. U_{EB} is the voltage between emitter and base, U_{EC} is the voltage between emitter and collector, I_{CE} is the current between collector and emitter electrodes etc.

First the polarization between the emitter and base electrodes will be examined, as a one-port electric cell. The recorded $U-I$ diagram is shown in Fig. 3. The characteristics are analogue to the solid state diode. The forward

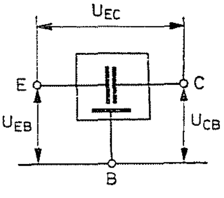

Fig. 2

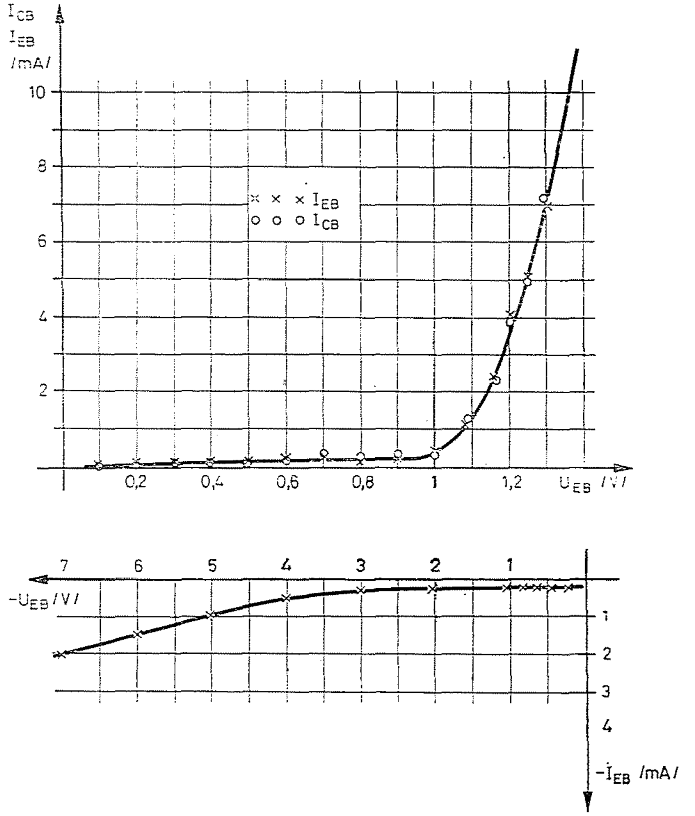

Fig. 3

resistance is 30 Ω, the backward resistance is about 2 kΩ. The result of the repeated measurements for collector and base electrodes is given as the same characteristics because of the symmetrical geometric and electric construction.

The second problem is to investigate the characteristics of the active two-port, i.e. the transistor characteristics. The experimental arrangement is shown in Fig. 4.

The applied max. voltage between the collector and emitter electrodes is one volt. The investigated characteristics is $I_{CE} = (U_{EB})$ with I_{EB} parameter. The $I_{EB} - U_{EB}$ characteristics is also examined at the constant $U_{CE} = 0.8$V.

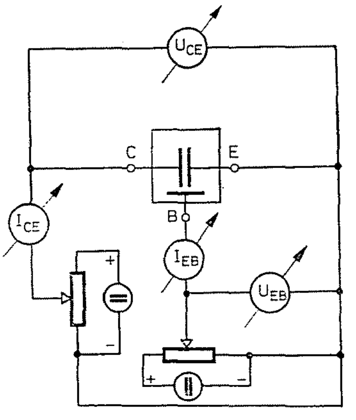

Fig. 4

3. Equivalent circuits of the electrolytic diode and transistor

Evaluation of the static characteristics

The equivalent circuit of the electrolytic diode and transistor may be constructed from the measured characteristics. The dynamic resistance of the electrolytic diode at 5 mA biase can be calculated as

$$\frac{\Delta U_{EB}}{\Delta I_{EB}} = \frac{0{,}15\ V}{0{,}005\ A} = 30\Omega \text{ on the forward}$$

characteristic.

The backward characteristics show only leakage current (0.2 mA) to -3V, and from here to the higher voltages a 2 kΩ resistance region follows.

The equivalent circuit constructed with the above data is shown in Fig. 5.

Hybrid parameters

Calculation of the hybrid parameters of the electrolytic transistor (from the measured characteristics) will be made as follows. The input resistance of the common emitter circuit is

$$h_{11e} = \frac{\Delta U_{EB}}{\Delta I_{EB}}, \quad \text{for} \quad U_{CE} = \text{const.}$$

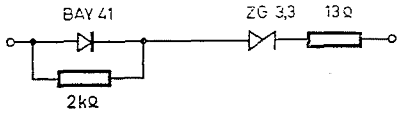

Fig. 5

From the characteristic $U_{EB} - I_{EB}$ biased to 70 μA:

$$h_{11e} = \frac{200\,\text{mV}}{0{,}1\,\text{mA}} = 2000\,\Omega.$$

The current to transfer ratio of the common emitter circuit:

$$h_{21e} = \frac{\Delta I_C}{\Delta I_B}, \quad U_{CE} = \text{const.}$$

From the $I_{CE} - U_{CE}$ characteristic biased to $I_C = 0.4$ mA ($I_B = 70\,\mu$A)

$$h_{21e} = \frac{\Delta I_C}{\Delta I_B} = \frac{0{,}08\,\text{mA}}{0{,}01\,\text{mA}} = 8\,.$$

The output conductivity of the common emitter circuit

$$h_{22e} = \frac{\Delta I_C}{\Delta U_{CE}}, \quad \text{for} \quad I_B = \text{const.}$$

can be determined from the slope of the characteristic $I_{CE} - U_{CE}$ biassed to $I_B = 70\,\mu$A

$$\frac{\Delta I_C}{\Delta U_{CE}} = \frac{0{,}35 - 0{,}32}{600} = 5.10^{-5} \text{ mho; corresponding to } \frac{1}{h_{22e}} = 20\,\Omega.$$

The modelling circuit constructed with above data is shown in Fig. 6. BFY 34 is used as the active two-port. The h_{21e} decreased by emitter resistor $R_E =$

$= 234\ \Omega$, input resistance h_{11e} is controlled by diode BAY 41 and series resistor R* = 2203 Ω, the output resistance is controlled by resistor R** = 20 kΩ.

The above value of the emitter resistor can be calculated from the voltage transfer ratio

$$A_U = -\frac{h_{21\text{cell}}}{h_{11\text{cell}}} \cdot R_t = -\frac{h_{21BFY} \cdot R_t}{h_{11BFY} + (1 + h_{21BFY}) \cdot R_E}$$

hence $R_E = 234\ \Omega$.

The input and output impedances can be calculated by means of the diagram.

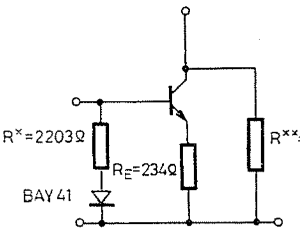

Fig. 6

4. The frequency response of the electrolytic cell

The frequency response of a transistor is limited by the time taken by carriers to diffuse from the emitter to the collector. In solid (Ge, Si) transistors, transit times are of the 10^{-7}—10^{-9} sec order. Since the mobilities of electrons and holes in semiconductor solid materials are at least 10^9 times higher than those of ions in solution, the transit time in the electrolytic transistor is one second or more.

The transient phenomena in the electrolytic cell have been measured by a DC oscilloscope. Qualitative investigation of the frequency response was carried out by square-wave pulses applied on the input of the cell. The rise-time and drop of the output wave-form are characteristic to the transient phenomena of the cell.

To obtain quantitative values, the Nyquist diagram of the cell has to be recorded by a VLF generator and a double beam oscilloscope. The frequency response and the phase diagram are shown in Fig. 7.

The frequency band-width of the cell as an amplifier network can be calculated from the rise-time

$$f = \frac{0{,}35}{t_2 - t_1} = \frac{0{,}35}{20{,}5} = 0{,}017 \text{ Hz}.$$

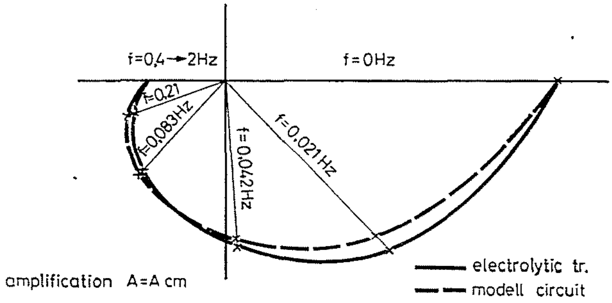

Fig. 7

The band-width measured on the Nyquist diagram (at 3 dB) is 0.02 Hz, closely approximating the above value. It means that the two methods give the same result.

5. The electronic model of the electrolytic cell

The equivalent circuit of the diode cell has been designed on the basis of the transient characteristics measured by oscilloscope. The same transient times will be exhibited by the circuit shown in Fig. 8.

The equivalent circuit of the two-port cell can be implemented if the following are considered.

Let us apply the principle of linear superposition to the circuit in Fig. 9 based on measured data. Two generators are driving the 1 kΩ load. One of them is the capacitive negative feed-back transistor amplifier, the other is the input generator through the capacitor C.

The Nyquist diagram of the capacitive negative feed-back amplifier is well known as characterizing the Miller integrator.

The Nyquist diagram of the generator active through the capacitor is well known as the differential (high-pass) network.

The linear graphic superposition in Fig. 10 will result in the theoretical Nyquist diagram closely approximating the recorded ones.

The passive R elements of the amplifier calculated from the static parameters are known. The value of the capacitor C will be determined from the band-width 0,02 Hz

$$C = \frac{1}{2\pi f R} = 8.10^{-3} = 8000\,\mu F.$$

It can be realized by two 4000 μF capacitors. The complete equivalent diagram corresponding to the static and dynamic characteristics is shown in Fig. 11. The recorded characteristics (Nyquist diagram) of the realized network are shown in Fig. 7 to be similar to the original one.

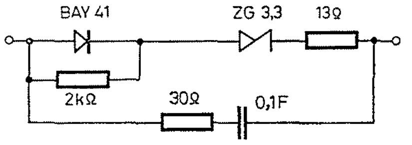

Fig. 8

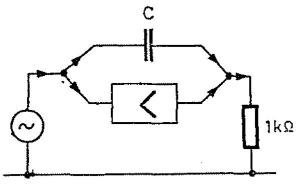

Fig. 9

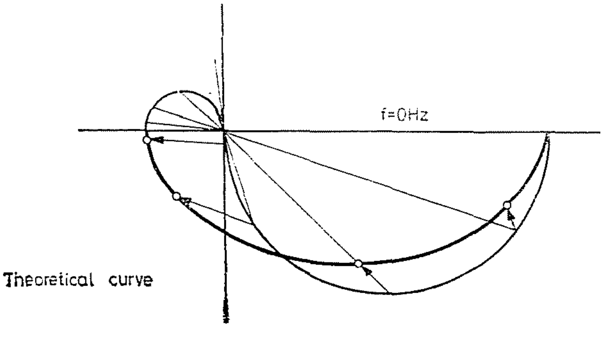

Fig. 10

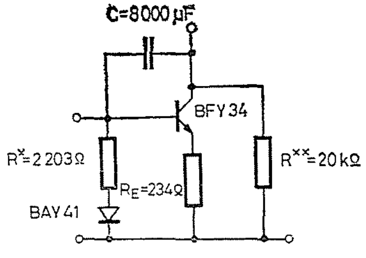

Fig. 11

The nonlinear distortion of the electrolytic amplifier is rather marked because of the different transit times of the polarization and depolarization (different rise- and fall times.

Summary

The behaviour of the electrolytic analogue transistor under conditions described above is basically as predicted. This extension of the phenomenon of the transistor action to the liquid state confirms the general applicability of the physical analysis of the semiconductor transistor.

The investigated till published transfer characteristics of the electrolytic cell are similar to those of the solid transistors only in the very low frequency range as proved by the recorded Nyquist diagram. The common emitter parameters/h_e were determined. The electronic model circuits have also been designed and tested.

The cell is likely of use for practically determining characteristics of electrochemical liquids (redoxi structures) and probably also of organic structures including living cells plasms.

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