

THE BEHAVIOUR OF SILVER CATHODES IN SOLID ELECTROLYTE FUEL CELLS

H. Tannenberger and H. Siegert

Institut Battelle, 7, route de Drize
1227 Carouge-Genève, SwitzerlandINTRODUCTION

Fuel cells with solid zirconia electrolytes which work at 750°C to 1000°C are promising systems to convert the chemical energy of cheap fossil fuels into electrical energy. Expensive platinum catalyst can be avoided because of the high working temperatures. Silver as the cathode material and nickel as the anode material have proved to be successful up to 900°C (1) (Fig. 1). In these fuel cells, the resistance of the electrolyte predominates in the total internal resistance of the cell, if the electrolyte has a thickness of more than 1 mm. To increase the power output per unit area of surface of the cell, the thickness of the electrolyte should be reduced. In so doing, polarisation phenomena become important.

This paper deals with the polarisation of silver electrodes. A tentative explanation for the observed phenomena will be given.

Polarisation phenomena in high temperature solid electrolyte fuel cells

A fuel cell with an oxygen-ion conductor as the solid electrolyte creates a voltage between its electrodes due to the difference of the oxygen partial pressure on both electrodes. This voltage is expressed by the Nernst equation :

$$E = \frac{RT}{4F} \ln \frac{P_{O_2}^K}{P_{O_2}^A}$$

If a current flows through a solid electrolyte fuel cell, the potential between the terminals will drop due to the internal resistance of the cell.

The internal resistance which limits the power output of the fuel cell can be divided into the following parts :

- polarisation of the cathode
- ohmic resistance of the electrolyte
- polarisation of the anode

The electrode polarisation thus defined contains all sorts of losses in the electrodes, such as the electronic resistance, diffusion resistance of the gases, activation polarisation and so on.

The voltage at the terminals of the fuel cell under load can then be expressed by :

$$V = E_o - V_C - V_{El} - V_A$$

V = Terminal voltage

E_o = Open circuit voltage

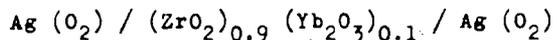
V_C = Polarisation of the cathode

V_{E1} = Ohmic voltage drop in the solid electrolyte
 V_A = Polarisation of the anode

The mechanism of the electrode polarisations is far from being understood. It is not yet even possible to determine unequivocally the voltage losses due to polarisation from the total internal resistance.

Current interrupting techniques are frequently used to separate electrode polarisation from the ohmic resistance of the electrolyte (2) (3).

We tried to obtain further information about polarisation phenomena by investigating cells of the type



with varying electrolyte thickness, which permits the determination of the influence of the electrolyte resistance on the total internal resistance more readily.

EXPERIMENTAL

Fig. 2 shows schematically the experimental set-up. The cell to be studied was made of a wafer of the electrolyte of ~ 30 mm diameter and about 3 mm thickness, held between two tubes made of steel.

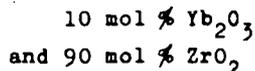
In the centre of the electrolyte wafer there was a hole, at the bottom of it was placed the one electrode, the other electrode being on the opposite side of the wafer. The surface of the electrodes was about 1 cm². By varying the depth of the hole, the thickness of the electrolyte between the two electrodes could be adjusted to the desired value.

Current collectors made of silver, were pressed against the electrodes by springs. Thermocouples were placed on both sides of the electrolyte wafer.

An oxygen stream of 100 cc/min was directed against both electrodes.

The electrical circuit, shown in Fig. 3, allowed measurement of the current-voltage characteristics of the cell. A current interruptor technique was used to measure the ohmic and the non-ohmic part of the total cell resistance. To do this a short time interruption relay (type Struthers-Dunn M1CC-C5-6.3 AC) was placed in the current circuit, which could break the current periodically for 0.4 milliseconds at a frequency of 100 cycles per second. The voltage-time curve was observed on an oscilloscope Tektronix type 503, and could be easily photographed.

As electrolyte, cubic zirconium dioxide of the composition of



was employed. The resistivity as a function of temperature of this composition is shown in Fig. 4. The electrolyte wafer was prepared by sintering a compact of the mixed oxide powders at 1900°C for 3 hours. The apparent density was about 92 % of the theoretical density and the wafers were gas tight.

The surface was prepared by rubbing with SiC paper, then rinsed with distilled water and heated at 1000°C for a short time.

Silver electrodes were prepared by painting 2 layers of a silver paste, Degussa Leitsilber 200, followed by a heat treatment up to 850°C.

RESULTS

Fig. 5 and Fig. 6 show typical characteristics of the cells. They are straight lines passing through the origin of the coordinates as they should, because the partial pressure on the two electrodes is the same :

$$P_{O_2}^C = P_{O_2}^A = 1 \text{ atm.}$$

At current densities higher than about 200 mA/cm² the characteristics begin to flatten out. This phenomenon, also observed by other workers (3), may be explained by the heating of the electrolyte due to the current flow. This hypothesis is supported by the fact, that the current density, above which the internal resistance of the cell decreases, depends on the thickness of the electrolyte and the nominal operating temperature.

We restrict further discussions to the linear part of the characteristics.

Fig. 7 shows the total resistance per cm² of cells having different electrolyte thicknesses, as a function of temperature. It is remarkable, that the temperature dependence of the total resistance of the cell is sensibly the same as that of the resistivity of the electrolyte, independently of the thickness of the electrolyte which varies by a factor of ten.

Fig. 8 shows a cross-plot of Fig. 7, that is the total resistance of the cell as a function of the thickness of the electrolyte at three temperatures. As can be seen, a residual resistance R_0 remains, if the thickness of the electrolyte is extrapolated to zero. The temperature dependence of R_0 is nearly the same as that of the resistivity of the electrolyte.

The separation of the total potential drop into the rapid ("ohmic") and slow ("non-ohmic") part by the current interrupting technique did not show a coherent result. It was not possible to relate the "non-ohmic" potential drop with the residual resistance R_0 .

DISCUSSION

The essential result of our measurement is, that we were able to determine the influence of the electrolyte resistance on the total resistance of the cell and so to define a total polarisation of the electrodes. This total polarisation, expressed by the residual resistance R_0 , depends on the temperature in approximately the same way as the resistivity of the electrolyte.

In the tentative explanation of the observed phenomena we shall assume, that the cathodic and anodic polarisation will be about the same, that is half of the observed total polarisation, and that the temperature is the same throughout the sample. Where these assumptions may alter significantly the interpretation, we shall discuss the possible consequences of a deviation from our assumptions.

At first, we may attempt to ascribe the residual resistance R_0 to a concentration polarisation at the cathode due to the diffusion of oxygen through a compact silver layer.

The potential drop due to concentration polarisation is

$$\eta = - \frac{RT}{2F} \ln (1 - j_1)$$

where

R = gas constant

T = absolute temperature

F = faraday constant

j_1 = limiting current density

The limiting current density can be expressed by

$$j_1 = \frac{4F C_o D}{d}$$

where

C_o = solubility of oxygen in silver

D = diffusion coefficient of oxygen in silver

d = thickness of the silver layer

Fig. 9 shows the potential drop η as a function of current density with the limiting current density as unity.

The characteristics of our cells are practically linear and never showed a tendency to limiting currents in the measured current range. If, nevertheless, we assume that the polarisation is due to the diffusion of oxygen in silver, and the limiting current density is much higher than the measured current density range and therefore the logarithmic behaviour of the concentration polarisation may approximate to the observed linear behaviour, theory predicts much smaller values for the polarisation e.g.

$$\eta = 13 \text{ mV}$$

$$\text{for } j = 0.25 j_1 \text{ at } 800^\circ\text{C}$$

than the observed polarisation, which is about

$$\Delta\varphi = 80 \text{ mV for } 200 \text{ mA/cm}^2$$

We may therefore exclude that concentration polarisation occurs in our cells.

Activation polarisation, involving losses associated with adsorption, or surface reactions, seems to us improbable at these high temperatures. In addition it would seem quite surprising that the temperature dependence of these losses should be the same as that of the resistivity of the electrolyte.

We propose therefore to explain the residual resistance by the fact that the electrodes are active only on discrete spots of small size, distant one from each other. In the case of molten salt fuel cells such a model has already been put forward (4).

The residual resistance, found by extrapolating the total internal cell resistance to zero electrolyte thickness, is then due to the loss of effective cross-section for the current flow through the electrolyte and the dependence of R_o on the temperature should be the same as that of the electrolyte resistivity. Fig. 10 shows schematically the dependence of the total internal cell resistance on the electrolyte thickness expected.

In the following a quantitative estimation of the dimensions of and the distance between the active spots will be given with the aid of simulating the element in an electrolytic tank.

To simplify the situation for the simulation we assume that the active spots have the form of parallel strips with constant width (Fig. 11).

The resistance of one "element", dependent on its thickness, was measured in the electrolytic tank. By putting in parallel n of these elements, the resistance of the unit area of the cell can be calculated.

Fig. 12 shows the simulated element in this electrolytic tank.

Fig. 13 shows the resistance \mathcal{R} of this element as a function of its thickness expressed by the parameter

$$\mathcal{L} = \frac{d}{\frac{p}{2}}$$

for a conductivity :

$$\rho = 1 \Omega \text{ cm}$$

and for a bath depth B :

$$B = 1 \text{ cm}$$

It is important to note, that the resistance \mathcal{R} can be expressed in the form of

$$\mathcal{R} = \mathcal{R}_0 + \mathcal{L}$$

for values of \mathcal{L}

$$\mathcal{L} \geq 1$$

independently of $\frac{b}{p}$. This means, that the current flow is homogenous above a distance d , where :

$$d \geq \frac{p}{2}$$

Fig. 14 gives the residual resistance \mathcal{R}_0 as a function of $\frac{b}{p}$.

The resistance R of an element with

$$\begin{array}{ll} \text{resistivity} & \rho \\ \text{and width} & B \end{array}$$

is then given by

$$R' = \frac{\rho}{B} \cdot \mathcal{R} = \frac{\rho}{B} \mathcal{R}_0 + \frac{\rho}{B} \cdot \frac{d}{\frac{p}{2}}$$

By putting $2n$ elements in parallel we get the resistance of a whole cell of length L and width B .

$$R = \frac{1}{2n} R'$$

Referring to Fig. 11 we have

$$n \cdot p = L \quad \text{or} \quad n = \frac{L}{p}$$

and obtain finally

$$R = \frac{\rho}{LB} \cdot \frac{p}{2} \cdot R_0 + \rho \cdot \frac{d}{BL}$$

In this formula the term

$$\frac{\rho}{LB} \cdot \frac{p}{2} \cdot R_0 = R_0$$

can be identified with the measured residual resistance R_0 we obtained by extrapolating the electrolyte thickness to zero (Fig. 8).^o

It should be noted, that from the knowledge of R_0 by experiment, it is not possible to determine p and b (from R_0) separately but only pairs of values p and b .

To interpret the results obtained at 800°C (Fig. 8), suppose that

$$L = B = 1 \text{ cm}$$

We can first calculate ρ of the electrolyte from the slope of the straight line in the diagram of total resistance versus electrolyte thickness. This yields

$$\rho = 28 \Omega \text{ cm}$$

in good agreement with the value of resistivity measured independently.

The residual resistance R_0 was

$$R_0 = 0.8 \Omega \text{ cm}^2$$

If we assume that the element behaves symmetrically with respect to its electrodes, we have, for instance, for the cathode

$$R_0^C = 0.4 \Omega \text{ cm}^2$$

and therefore

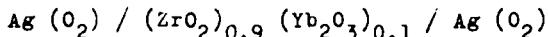
$$R_0 = 0.4 = \frac{\rho}{LB} \cdot \frac{p}{2} \cdot R_0$$

From this and Fig. 14 we can calculate the following table :

p (μ)	400	100	40	20
b (μ)	88	1.7	$180 \cdot 10^{-4}$	$6 \cdot 10^{-4}$

CONCLUSIONS

The hypothesis that the silver electrodes are active only on discrete spots, the one distant from the other, is able to explain the observed dependence of the total resistance of the cell



on the thickness of the electrolyte. As the residual resistance R_0 in this model is directly linked to the electrolyte, its temperature dependence should be the same as that of the resistivity of the electrolyte.

The quantitative evaluation of the data shows that the dimensions of the active spots become very small if the distance between them decreases.

Local overheating of the active spots, lowering the resistivity of the electrolyte in their vicinity, would yield still smaller dimensions for the spots having the same distance.

Conforming to Figs 8 and 13 we must admit, that the maximum distance between the spots should be less than about 500μ .

It is evident, that the model of the strips employed for the simulation does not correspond to reality. Certainly, the active spots are of irregular shape and are distributed irregularly over the electrode surface. However, the order of magnitude of b and p , calculated on the basis of our experimental value of R_0 , would not be altered by orders of magnitude.

There remains the question of how to interpret the "non-ohmic" part of the total potential drop. We would suggest, that the phenomenon, yielding the "slow" potential drop, also lies in the electrolyte.

At least for the cathodic polarisation, it may be suggested that the electrolyte region below the active spot is slightly reduced by the cathodic current. If the current is interrupted, the open circuit potential corresponds in the first instant to the chemical potential of oxygen in the slightly reduced electrolyte. After having interrupted the current the reduced region of the electrolyte below the active spots is reoxidized by the oxidizing atmosphere in the cathode compartment and the initial open circuit potential will slowly re-establish itself.

REFERENCES

- 1) "Comportement d'anodes en nickel dans les piles à combustible à électrolyte solide"
H. Schachner, H. Tannenberger.
Revue "EPE", Vol. II, N° 1, 1966
- 2) "Investigation of the polarisation of electrodes in solid electrolyte cells"
A.T. Filjaev, C.F. Palguyev, C.V. Karpatchev
Akademia Nauk SSSR. Uralskii Filial, Trudi instituta electrochimii 1961, 2, (p. 199-209)
- 3) "Testing of electrodes for high temperature solid electrolyte fuel cells"
E.F. Sverdrup, D.H. Archer, J.J. Alles, A.D. Glaser
Proc. of the Symposium on Hydrocarbon Air Fuel Cells 2, N° 3, part 2 (1965)
- 4) "High temperature fuel cells"
E. Gorin, H.L. Recht
Fuel Cells (W. Mitchell ed.) Academic Press, p. 193, (1963)

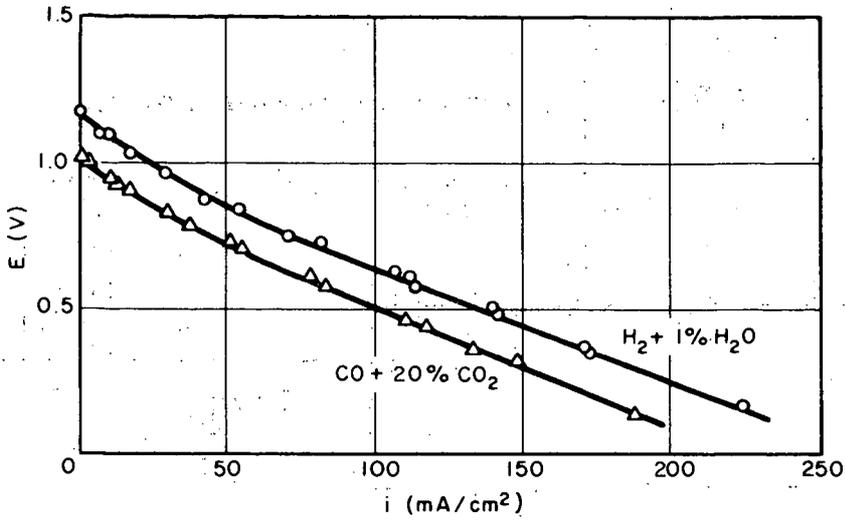


Fig. 1 Performance of solid electrolyte cell
 $Ag / (ZrO_2)_{0.9} (Yb_2O_3)_{0.1} / Ni$
 $T = 800^\circ C$, electrolyte thickness : 1.5 mm

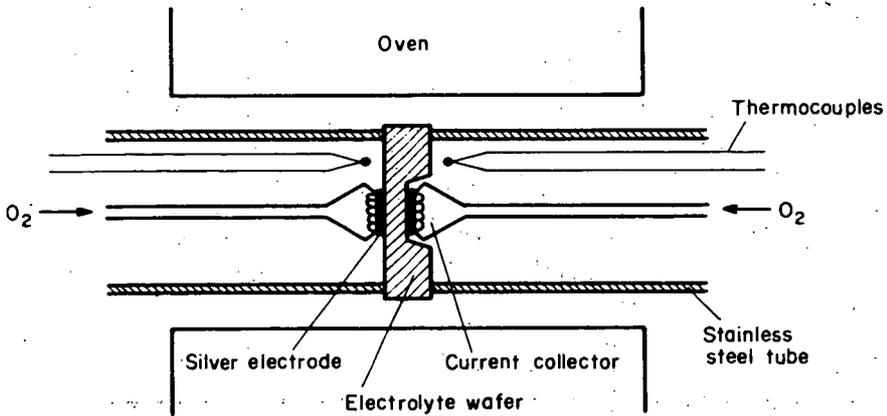


Fig. 2 Experimental set-up of the solid electrolyte cell
 $Ag(O_2) / (ZrO_2)_{0.9} (Yb_2O_3)_{0.1} / Ag(O_2)$

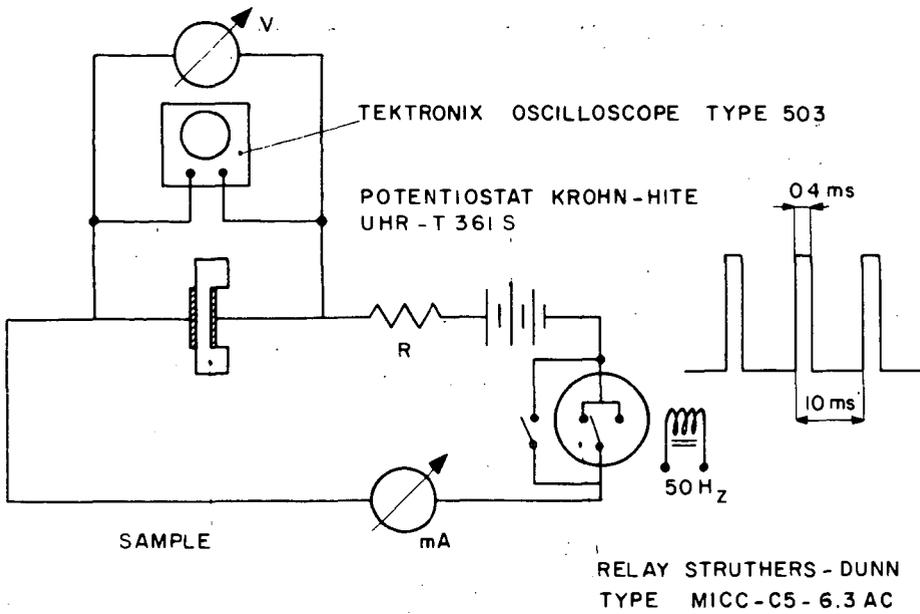


Fig. 3 Electrical measuring circuit

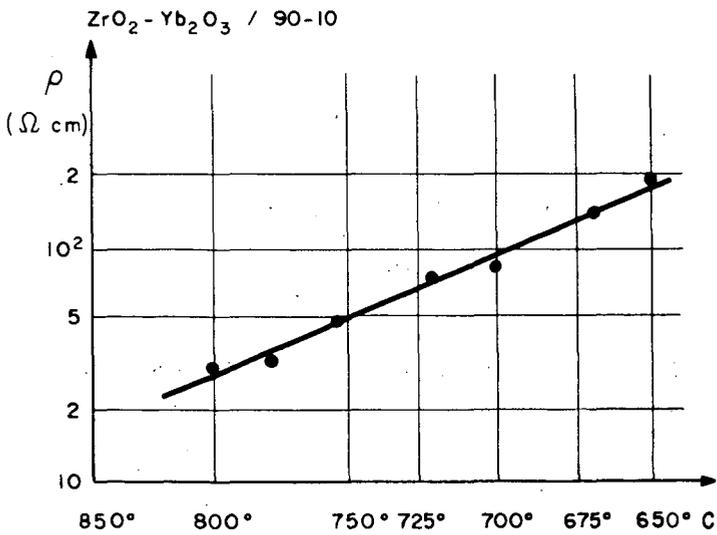


Fig. 4 Resistivity of the electrolyte $(\text{ZrO}_2)_{0.9}(\text{Yb}_2\text{O}_3)_{0.1}$ as a function of temperature

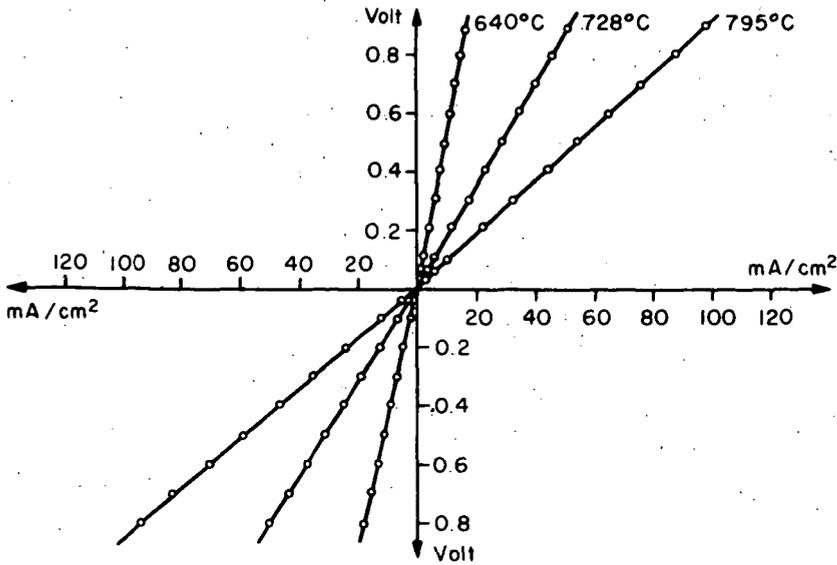


Fig. 5 Characteristics of the cell :
 $\text{Ag}(\text{O}_2) / (\text{ZrO}_2)_{0.9} (\text{Yb}_2\text{O}_3)_{0.1} / \text{Ag}(\text{O}_2)$
 Electrolyte thickness : 3.65 mm

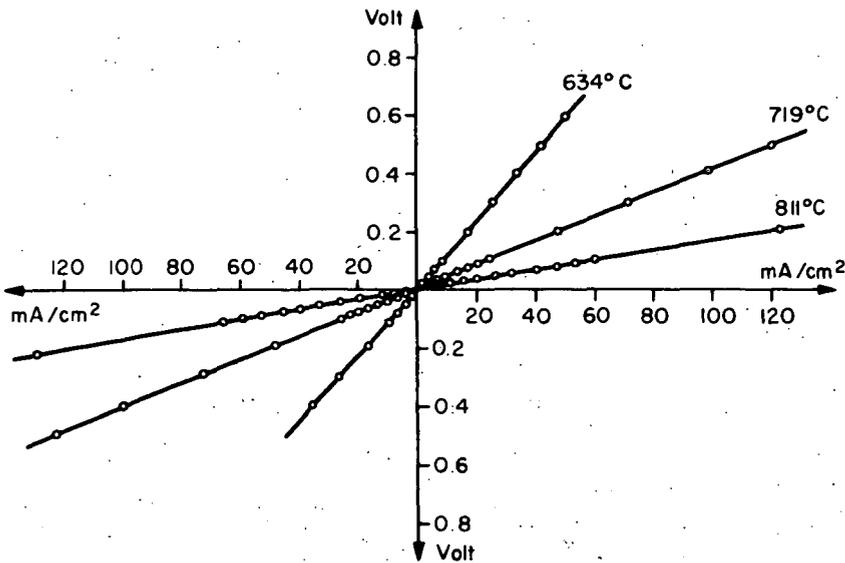


Fig. 6 Characteristics of the cell :
 $\text{Ag}(\text{O}_2) / (\text{ZrO}_2)_{0.9} (\text{Yb}_2\text{O}_3)_{0.1} / \text{Ag}(\text{O}_2)$
 Electrolyte thickness : 0.38 mm

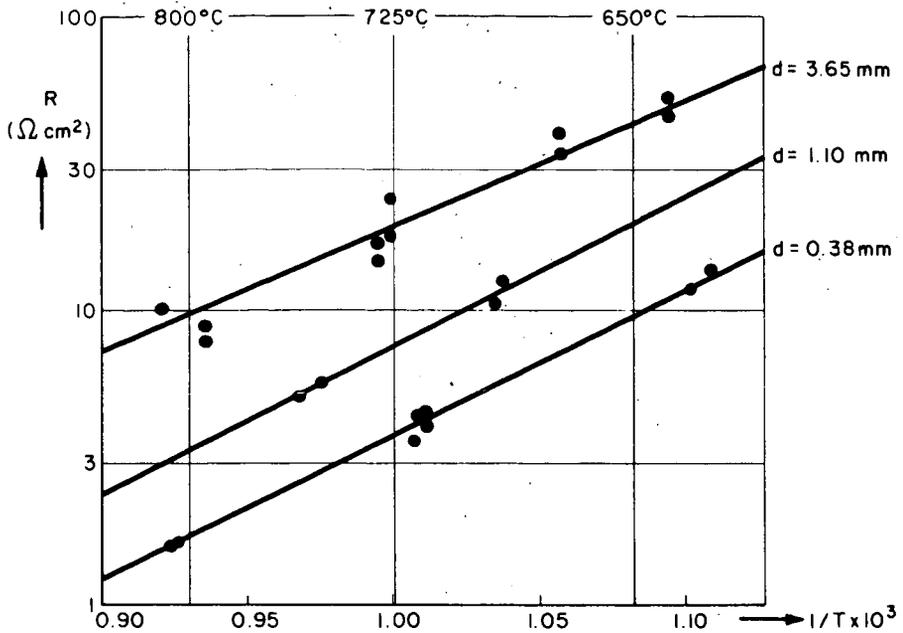


Fig. 7 Total internal cell resistance of three cells with different electrolyte thickness as a function of temperature

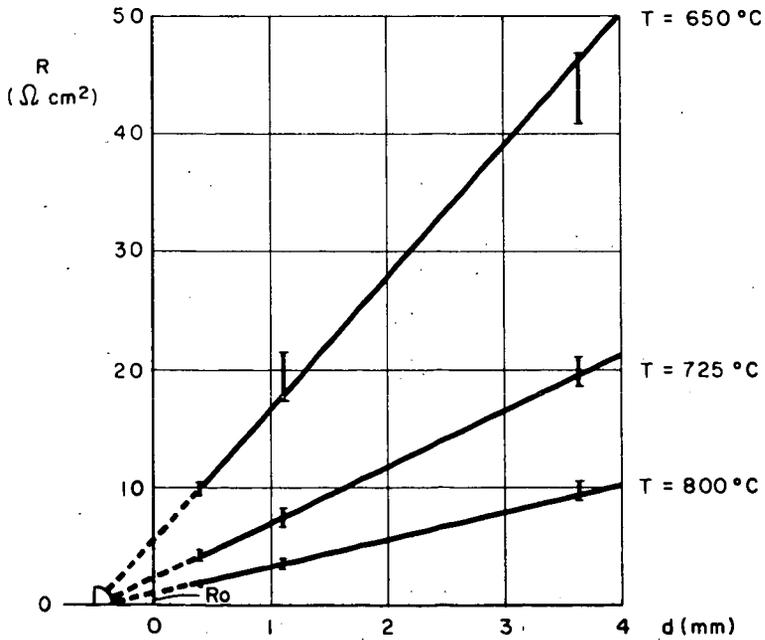


Fig. 8 Total internal cell resistance as a function of electrolyte thickness d at three temperatures

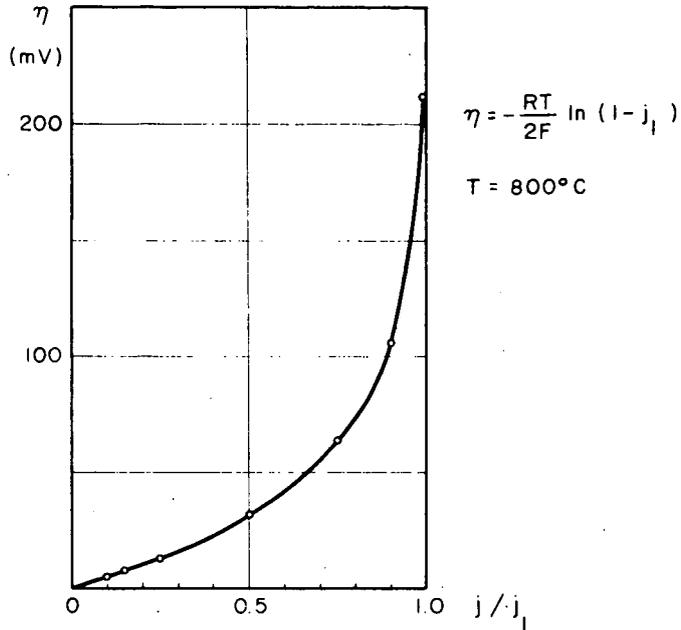


Fig. 9 Concentration polarization as a function of current density in units of the limiting current density j_l .

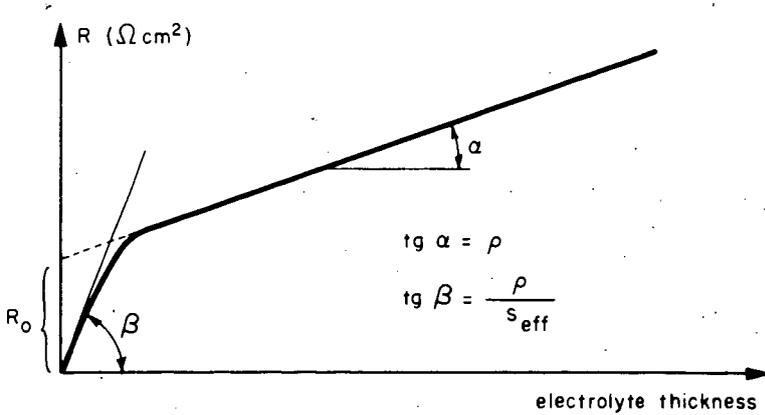


Fig. 10 Total internal cell resistance as a function of electrolyte thickness for a cell having electrodes being active only on isolated spots.

ρ electrolyte resistivity
 s_{eff} effective electrode area per cm^2
 (Area of the active spots).

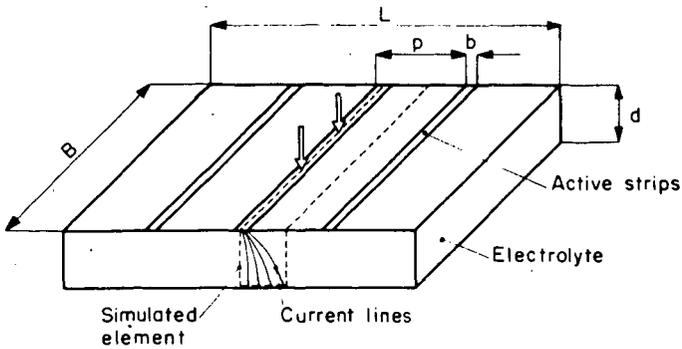


Fig. 11 Model for the simulation of the electrode
 L length, B width, d thickness of the electrolyte,
 p distance between "active strips", b width of
the "active strips"

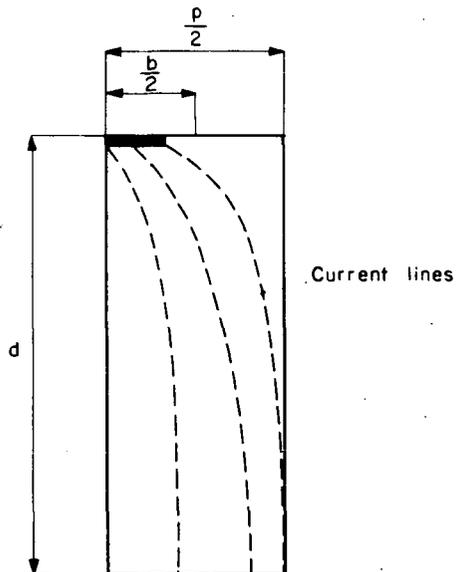


Fig. 12 Simulated single "element"

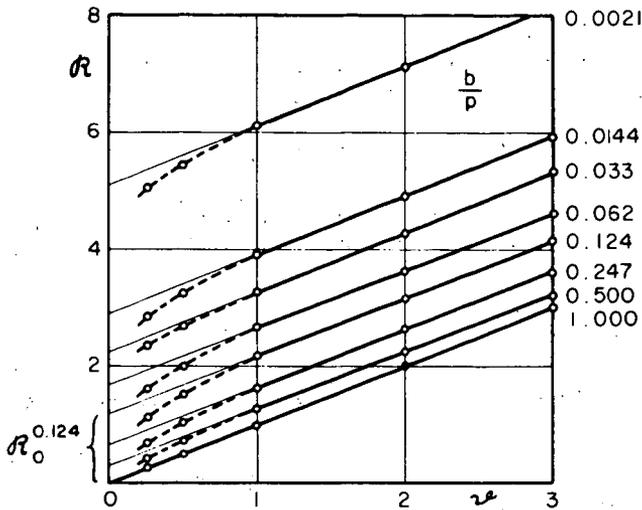


Fig. 13 Resistance R of the simulated single "element" as a function of the thickness parameter $v = \frac{d}{p}$ for different values $\frac{b}{p}$ (width of active strips)

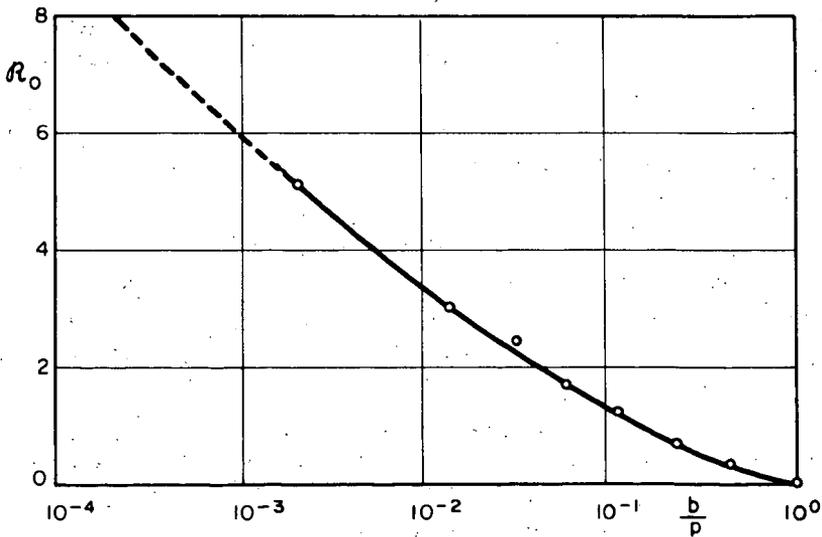


Fig. 14 Residual resistance R_0 as a function of width of active strip $\frac{b}{p}$