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Comparison of electrode impedances of Pt, PtIr (10% Ir) and Ir-AIROF electrodes used in electrophysiological experiments

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Abstract—*In tissue impedance measurements with the 4-electrode assembly, unexpected difficulties may occur because a combination of electrode impedance and stray capacitance in the array of four electrodes, can lead to serious measuring failures in the low-frequency range. An optimal solution to this problem can be obtained if the electrode impedances are frequency independent. A comparative study of the electrode impedances of Pt and PtIr electrodes and of a new electrode material (Ir-AIROF) is reported. It is shown that the impedance of Ir-AIROF electrodes is relatively low and almost frequency independent. Therefore the use of Ir-AIROF electrodes provides a solution to the problem mentioned above.*

Keywords—*Electrode impedance, Four-electrode assembly, Iridium electrodes, Tissue impedance*

1 Introduction

IN ELECTROPHYSIOLOGICAL experiments where small electrodes are used, electrode impedances may be a serious problem. Measurement of relatively high-frequency components requires an amplifier with high input resistance combined with a low input capacity (including the input wires). For measurements of action potentials using 25 μm diameter Pt electrodes these requirements can reasonably be met by means of bootstrapping and/or negative input capacitance adjustment of the amplifiers. However, unexpected difficulties can occur in tissue-impedance measurements, where the so called 4-electrode arrangement has to be used. In this case frequencies are investigated in the range of 10 Hz to 30 kHz (frequency spectrum of action potentials). In these experiments the combination of varying electrode impedances and stray capacitances in the array of 4-electrodes can result in serious deviations in the low-frequency range. This effect can be illustrated by means of a calibration of the 4-electrode assembly in a saline solution (9 g NaCl/l), which shows an apparent frequency dependence below 1 kHz (see Fig. 2). It is known, however, that the electrical impedance of saline solutions is independent of the frequency in this range. This frequency dependence can be explained by considering the model given in Fig. 1.

The current source injects, by means of electrodes 1 and 2, a current 'i' through a saline solution with resistance R-saline, while the amplifier A measures the resulting voltage over R-saline by means of the electrodes 3 and 4. The current i also develops a voltage over Z_{e_1} and Z_{e_2} which increases at low frequencies because of the frequency dependence of the electrode impedances (DE BOER and VAN OOSTEROM, 1978). This voltage is coupled to the measuring electrodes by way of the stray capacitance C_s between the electrode wires.

In the model of Fig. 1, two current paths are important. First the desired current path along a, b, c, d and second the undesired current path along a, e, b, c, f, d. The voltage V, measured by the

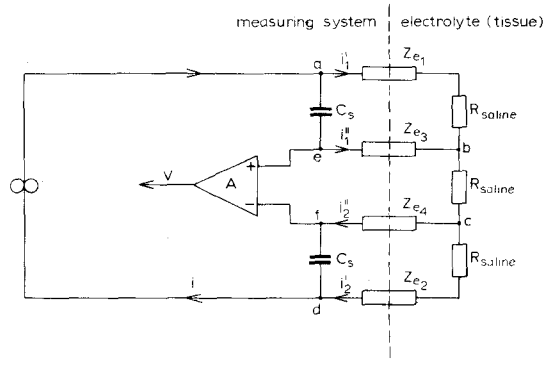

Fig. 1 *Model of 4-electrode assembly to measure R-saline, with current injection electrode (1) and (2), voltage measuring electrodes (3) and (4), stray capacitances C_s and electrode impedance Z_e ($i'_1 + i''_1 = i$ and $i'_2 + i''_2 = i$)*

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amplifier A can be written as: $V = (iR_{saline}) + (i_1''Z_{e3}) + (i_2''Z_{e4})$ (i) in which (iR_{saline}) is the desired voltage and $(i_1''Z_{e3}) + (i_2''Z_{e4})$ (ii) is the undesired voltage.

If we take for simplicity $Z_{e1} = Z_{e2} = Z_{e3} = Z_{e4} = Z_e$, (iii) then the following expression for V can be derived:

$$V = \frac{2Z_e(Z_e + R_{saline})}{\underbrace{\frac{1}{j\omega C_s} + (2Z_e + R_{saline})}_{\text{undesired}}} \underbrace{i + (R_{saline} i)}_{\text{desired}} \qquad \text{.(iv)}$$

where

$\frac{1}{j\omega C_s}$ = (Complex) impedance of the stray capacitance C_s.

$Z_e = \frac{k}{(j\omega)^{0.75}}$ for platinum electrodes (DE BOER and VAN OOSTEROM, 1978);

k = constant.

Thus it can be seen that Z_e increases with decreasing frequency; therefore the contribution of the undesired part of the voltage V, measured with the amplifier A will increase with decreasing frequency. Experimental results in which this effect is obvious are given in curve *a* of Fig. 2.

The model of Fig. 1 has been described in more detail by VAN OOSTEROM *et al.* (1979), who also suggested some solutions to this problem. From the simple model of Fig. 1 it can be seen that minimisation of the stray capacitance C_s improves the results but this minimisation has practical limitations. Using PtIr (10% Ir) electrodes (100 μm diameter and inter-electrode distances of 500 μm) with the shortest possible electrode wires, the effect is not sufficiently suppressed. A further improvement can be obtained by decreasing the electrode impedances Z_e. This can be done by enlarging the surface area of the electrodes by electrolytic etching. The combined effects of minimisation of the stray capacitances and decreasing the electrode impedances can be seen in Fig. 2, curve *b*.

It can be seen from the description given by VAN OOSTEROM *et al.* (1979) and from the simplified model given in Fig. 1, that optimum performance would be obtained if the electrode behaved as a pure resistor over the whole frequency range. From the literature (DE ROOIJ and BERGVELD, 1980) it is known, that the pH-sensitive Ir-AIROF electrodes are almost resistive, at least for relatively large electrode areas. This paper reports an investigation of the applicability of this type of electrodes in the 4-electrode assembly, using small electrode areas. The preparation of these electrodes is described and experimental results are compared with those obtained using the conventional Pt and PtIr electrodes. The results of impedance measurements in a saline solution, with Ir-AIROF electrodes are shown in Fig. 2 as curve *c*. From Fig. 2 it can be concluded that with the new electrode material (Ir-AIROF), the

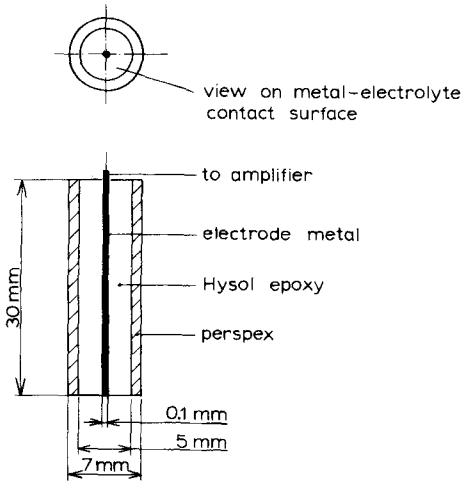


Fig. 3 *Diagram to show construction of the electrodes from which the electrode impedances were determined*

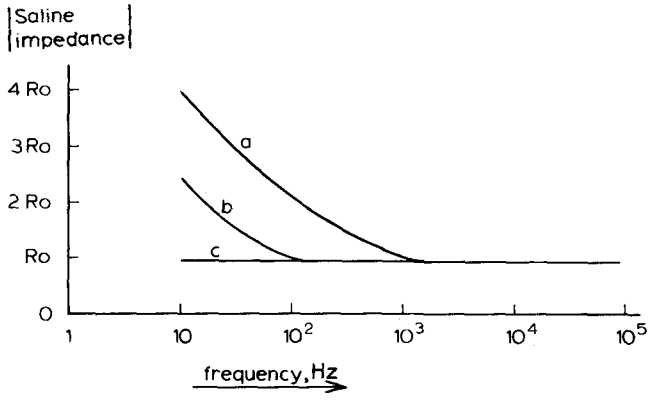


Fig. 2 *Typical values of the impedance of a saline solution (9 gr NaCl/1).*
(*a*) *Impedance characteristics measured with original electrode design.*
(*b*) *Impedance characteristic measured with an electrode design in which stray capacitances were minimised. (Pt Ir (10% Ir) electrode material). In addition the electrode impedances were minimised by electrolytic etching.*
(*c*) *Impedance characteristics measured with Ir-AIROF electrodes*

problems occurring in tissue impedance measurements as discussed above can be avoided.

2 Construction and preparation of the electrodes

Since the aim of this study was to compare the electrode impedances of two commonly used electrode materials (Pt and PtIr (10% Ir)) with a new electrode material (Ir-AIROF), it was essential that the geometry of the contact areas of all three types was identical. Furthermore it was desirable to use very pure metals to avoid possible effects on electrode impedance owing to impurities. For tissue impedance measurements 100 μm diameter metal wires were used. The same sized wires were also used for comparison of electrode impedances. The metal electrodes were embedded in a Hysol Epoxy (Resin C8–W795; Hardener H–W796) in the centre of a perspex cylinder (7 mm o.d.; 5 mm i.d.) (see Fig. 3). The electrode surfaces were polished and cleaned in an ultrasonic cleaning bath containing ethanol. Microscopical examination (magnification 40×) of the electrode surfaces showed no geometrical differences between the three electrodes.

It is known that electrolytic etching enlarges the effective surface of electrodes, resulting in lower electrode impedances (BUCHTHAL *et al.*, 1957). In our study etching was achieved by applying a sinusoidal voltage between the electrode and a large indifferent Pt-ringelectrode both immersed in a saline solution (9g NaCl/l). The amplitude of the voltage was increased until gas bubbles appeared at the metal-electrolyte surface. It appears that an amplitude of 1·5 V and a frequency of 10 Hz are appropriate parameters for the voltage applied to the electrodes for one min. This etching procedure was used for all three electrode materials under investigation. The electrode impedances were measured directly after etching (see Section 4). With respect to the Ir-electrodes a specific electrochemical technique was used to further reduce the electrode impedance. This technique has been described fully by DE ROOIJ and BERGVELD (1980) and only a short description is given here. Its effects on Pt and PtIr (10% Ir) are unknown and in the present study it was used to prepare all three metals (Pt, PtIr, Ir).

The electrode under preparation was immersed in a 0·5 M H_2SO_4 solution at room temperature (20 ± 2°C) as shown in Fig. 4.

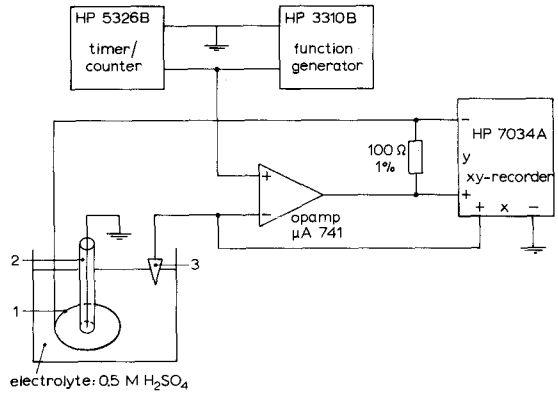


Fig. 4 *Experimental set-up for the preparation of Ir-AIROF electrodes*
1 = *large platinum ring used as reference electrode*
2 = *electrode to be prepared*
3 = *saturated calomel electrode*

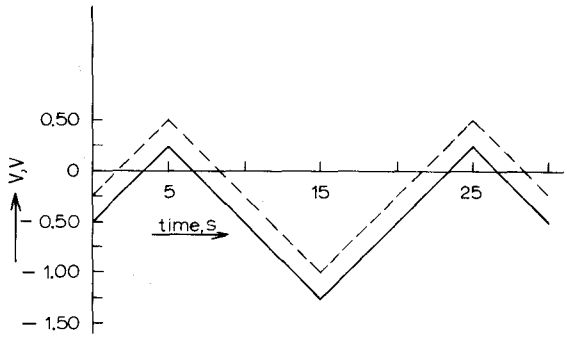


Fig. 5 *Potential used for preparation of Ir-AIROF electrodes*
——— *potential of the electrolyte*
– – – *potential measured with the calomel electrode*

A triangular voltage (see Fig. 5) was applied between the electrode and the electrolyte. In the case of Ir containing electrodes this results in the growth of a Ir-oxide layer which is called 'Anodic Iridium Oxide Film' (Ir-AIROF) (GOTTESFELD *et al.*, 1978; GOTTESFELD and MCINTYRE, 1979). The thickness of the layer can be monitored by a so called voltammogram as shown in Fig. 6 *a*, *b* and *c*.

For the preparation of Ir-AIROF electrodes a triangular voltage of −1·25 to +0·25 V had to be applied between the electrolyte and the electrode under preparation (GOTTESFELD and MCINTYRE, 1979). This voltage was measured by means of a saturated calomel electrode (see Fig. 4). The constant voltage drop over this electrode was +0·25 V. Thus with the amplifier used as a voltage follower, the potential of the function generator had to vary between −1·0 V and +0·5 V (see Fig. 5). The number of periods of the triangular voltage was detected by the HP 5326B. On the *xy*-recorder the voltage measured with the calomel electrode was recorded on the *x*-axis, and the current through the electrode under preparation on the *y*-axis, which provided the voltammogram as given in Fig. 6 *a*, *b* and *c*. The voltammogram shows the relation between the applied voltage and the resulting current, thus in fact the value of the corresponding electrode impedance.

This means that, if a sequence of cycles shows increasing current values (opening of the voltammogram), the electrode impedance is decreasing. So by means of a voltammogram the process of the decrease of the electrode impedance can be monitored.

Instead of a triangular voltage of 0·05 Hz a square-wave voltage of 0·5 Hz can be used to reduce the time of preparation of Ir-AIROF electrodes. Voltammograms however can only be recorded with a triangular voltage.

The voltage limits for the square-wave voltage were the same as for the triangular voltage. The most stable Ir-AIROF electrodes were prepared if the process was stopped at the positive maximum of the voltage used.

3 Experimental arrangement for electrode impedance measurement

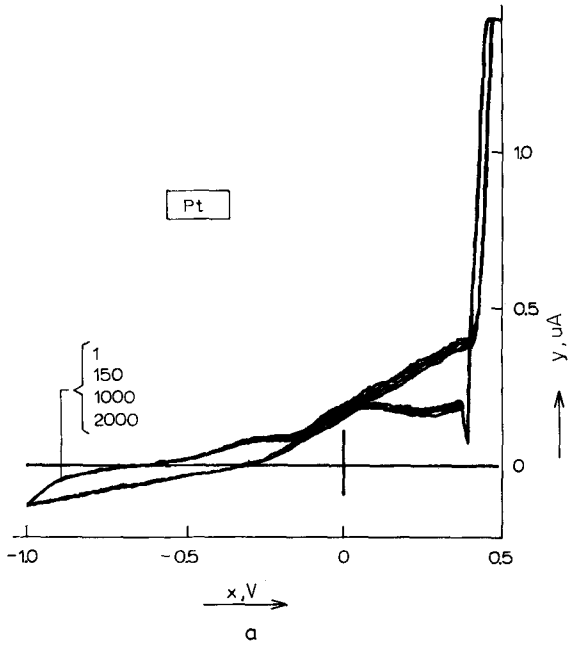
E.M.G. signals contain frequency components between 10 Hz and 30 kHz. To investigate the relation between measured e.m.g. activity and tissue impedance, the tissue impedance should be measured within the same frequency range. The experimental set-up for electrode impedance measurements is shown in Fig. 7. The most important specifications of the preamplifiers used were the following:

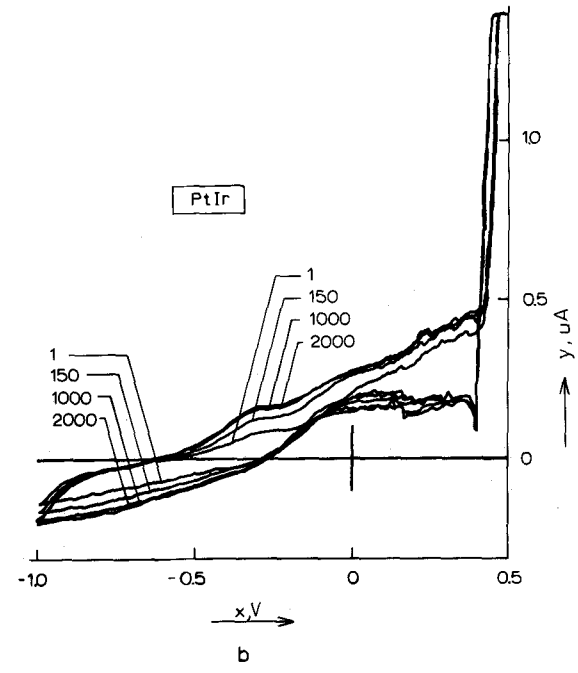
Input impedance including 20 cm coax. cable:
200 MΩ||0·3 pF;

Bandwidth:
0 Hz–130 kHz (−3 dB);

Common mode rejection ratio:
>60 dB (0 Hz–30 kHz).

The measurements of the various electrode impedances were carried out using sinusoidal currents with a constant amplitude. It is known that the





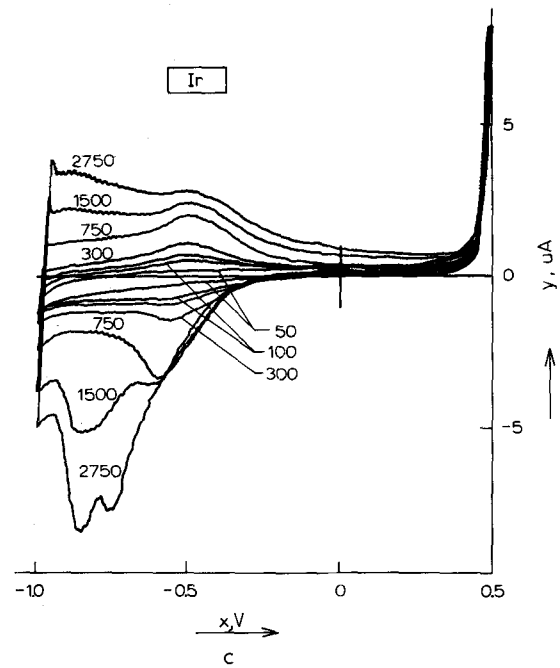


Fig. 6 *Typical voltammograms of Pt, PtIr and Ir electrodes. The parameter is the number of periods of the triangular voltage used before recording of the voltammogram*

electrode impedance depends on the current density through the electrode/electrolyte surface. For this reason the current density was chosen within the so

4 Results

The measurements of the impedance of electrodes which were only polished and cleaned in an ultrasonic

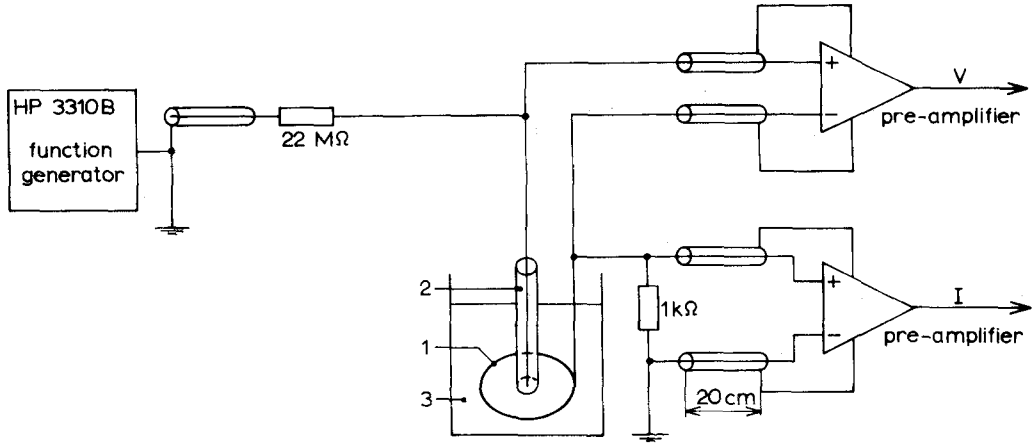


Fig. 7 *Experimental set-up for the determination of electrode impedances*
1 = large platinum ring
2 = electrode under investigation
3 = saline solution: 9 g NaCl/l temperature 20°C ± 1°C

called limits of linearity of the electrode impedance (SCHWAN, 1968). For the 100 μm diameter electrodes this meant that a current amplitude of 0·25 μA ($\approx$ 30 A/m^2) was used. The voltage response of the electrode to a square-wave current with a repetition frequency of 100 Hz and 10 kHz was investigated with the same set-up as shown in Fig. 7. This illustrates in a more direct way the capacitive and resistive components of the electrode impedance (BLOCK, 1968).

cleaning bath, are shown in Table 1. Mean values and standard deviation (σ) were calculated from 15 measurements per frequency.

The electrode impedances measured in a saline solution after electrolytic etching (9 gr NaCl/l) are shown in Table 2.

Notice the large decrease in impedance of the Ir-electrode and the smaller reduction of the PtIr-electrode. However, the low impedances of PtIr and Ir appear to be instable. After two days of storing

Table 1. Mean values and standard deviations (σ) of measured electrode impedances (15 measurements per frequency per electrode type) using sinewave

	Pt		PtIr		Ir	
Frequency	Mean	σ	Mean	σ	Mean	σ
Hz	kΩ	kΩ	kΩ	kΩ	kΩ	kΩ
10	1348	72	1300	63	791	73
100	277	42	275	30	235	17
1 000	43	10·2	48·2	2·1	48·3	2·4
10 000	7·6	1·5	7·50	0·36	8·00	0·54
100 000	3·83	0·29	3·57	0·07	3·53	0·13

Table 2. Mean values and standard deviations of electrode impedances after simple electrolytic etching (10 measurements per frequency)

	Pt		PtIr		Ir	
Frequency	Mean	σ	Mean	σ	Mean	σ
Hz	kΩ	kΩ	kΩ	kΩ	kΩ	kΩ
10	1 288	32	600	73	65	6·5
100	226	12	105	13	22·1	1·2
1 000	32·28	0·10	19·83	0·20	10·14	0·09
10 000	6·18	0·10	5·10	0·14	3·76	0·23
100 000	3·92	0·12	3·58	0·07	3·42	0·04

in demineralised water the electrode impedances returned about 80% of the original (pre-etching) values.

The electrode impedances measured after electrode preparation according to the method described for Ir-AIROF electrodes are shown in Table 3. The impedances of Pt and PtIr electrodes were rather unstable, while the values did not show, on average, either a decrease or an increase. However, the electrode impedance of Ir was stable with time, and the values were greatly decreased, especially in the low-frequency range.

As already mentioned, the characteristics of the electrode impedance can be shown in a more direct way by means of the voltage response of the electrode to a square-wave current. If the electrode impedance is resistive, the voltage response will also be a square wave, as is nearly the case with Ir-AIROF at 10 kHz (see Fig. 8). If the electrode impedance is capacitive, the voltage response will be a triangle, as is almost the case with Pt at 100 Hz (see Fig. 8).

5 Discussion

Compared with Pt and PtIr electrodes, Ir-AIROF electrodes have a much reduced impedance in the low-frequency range. Furthermore, the Ir-AIROF impedance is much less frequency dependent than that of Pt or of PtIr.

A difference between the preparation of large Ir-AIROF electrodes (DE ROOIJ and BERGVELD, 1980) and small Ir-AIROF electrodes (this paper), is the number of cycles of the triangular voltage necessary to open the voltammograms (see Fig. 6), which correlates with a reduction of the electrode impedance. For large electrodes 200 cycles appear to be sufficient, while for small electrodes as described in this paper about 2000 cycles appear to be necessary to open the voltammograms. For this difference we have no explanation till now.

Table 3. Mean values and standard deviations of measured electrode impedances after Ir-AIROF preparation procedure (10 measurements per frequency)

Frequency	Pt		PtIr		Ir	
	Mean	σ	Mean	σ	Mean	σ
Hz	kΩ	kΩ	kΩ	kΩ	kΩ	kΩ
10	1040	120	750	110	9·28	0·17
100	330	77	151	19	6·25	0·10
1000	72	16	27·91	0·37	5·28	0·09
10000	13·4	3·9	6·59	0·61	4·98	0·08
100000	6·2	2·5	4·17	0·11	5·58	0·09

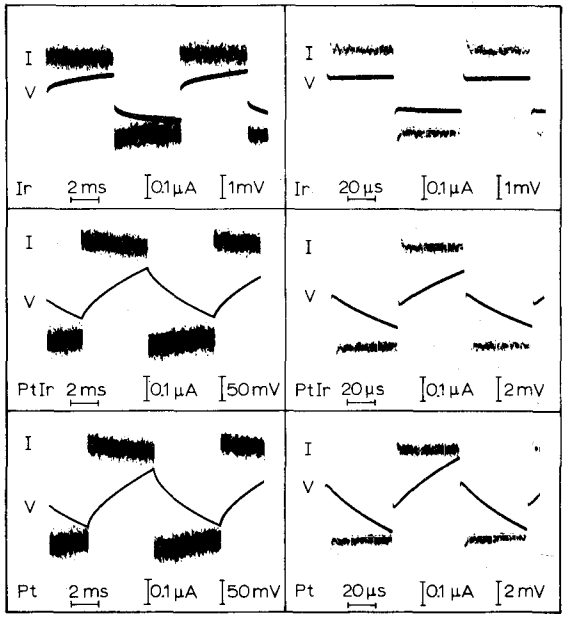


Fig. 8 *Voltage responses of the electrode to a square-wave current with different repetition frequencies (100 Hz and 10000 Hz). (Response after Ir-AIROF type preparation; notice the different voltage scales.)*

It has also been shown in this paper that electrolytic etching reduces the impedance of Ir electrodes by a larger amount than for the other electrode materials. However, no stable electrode impedances could be obtained with this procedure, probably because no stable Ir-oxides were formed by this process.

The final conclusion is that Ir-AIROF electrodes are excellent for tissue impedances measurements and are free from the undesirable influence of high impedances in the low-frequency range, as shown in curve *c* of Fig. 2. The mainly resistive character of the material, low impedance and good mechanical properties of Ir-AIROF electrodes offer many advantages for electrophysiological measurements. By means of specific etching techniques, it is possible to make very small needle shaped Ir-electrodes (diameters down to about 0·1 μm can be obtained) with considerable mechanical strength and relatively low impedance. In addition, large Ir-AIROF electrodes can be used as reference electrodes and have a lower impedance than Ag/AgCl-electrodes (DE ROOIJ and BERGVELD, 1980).

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