Tyco Laboratories, Inc.
Bear Hill
Waltham, Massachusetts 02154

DEVELOPMENT OF CATHODIC ELECTROCATALYSTS FOR USE IN LOW TEMPERATURE H_2/O_2 FUEL CELLS WITH AN ALKALINE ELECTROLYTE

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I. SUMMARY

During this month 14 compact samples have been investigated for activity as O_2-reduction catalysts in 2 N KCH at 75°C. Of these, four were carbides, which show some activity for O_2-reduction, but have too high corrosion rates at the potentials of interest ($E \geq 900$ mv); the other ten were borides. All the borides tested show high corrosion in the relevant range of potentials. Activity for O_2-reduction was not measured for the borides because of their high corrosion rates.

Simultaneously with the measurements of corrosion resistance and catalytic activity of compact samples, highly dispersed catalysts are being prepared and tested in the "floating electrode" cell. Highly dispersed carbides are being prepared both by carburization with CO and by decomposition of salts of organic acids (such as the iron salt of mellitic acid). In addition, Ag electrodes have been prepared by sintering highly dispersed AgO with Teflon and reducing in situ at the working potential. Co-deposits of PtAu and PdAu have been prepared by reducing solutions of Pt-Au and Pd-Au salts with sodium borohydride.

The floating electrode cell has been used to measure the performance of three commercial Pt-Teflon electrodes in O_2-reduction and H_2-oxidation, with the purpose of obtaining reference i (E)-curves. A fast interruption technique to measure the iR-drop has been developed and used with the floating electrode.

Three pasted, screen electrodes based on Ag and one based on Fe_2C-Fe_3C powder have also been studied using this apparatus.

II. TEST OF COMPACT SPECIMENS

Graphite (Fig. 1)

This material has been tested again, using a graphite counter electrode and a static hydrogen reference electrode (separated

from the main compartment through a hydrophilic Teflon frit). The purpose of this measurement was to determine again if the same activity for O_2 obtained in a system free of Pt is the same as in the system with Pt counter-electrode immersed in the working electrolyte. The result is essentially the same as that published in the second quarterly report which is a reassurance that the measured activities are not falsified by Pt.

Carbides

TiC (Fig. 2): This material corrodes above E = 0.9 volt. Below this potential, activity for O_2-reduction exists.

Cr_3C_2 (Fig. 3): Although corrosion is clear at E > 300 mv in the curve taken with increasing potential, the electrode passivates with treatment at positive potentials (corrosion starts then at E > 800 mv). Activity for O_2-reduction is relatively high.

WC-Co (Figs. 4 and 5): These materials show excessive corrosion.

Borides (Figs. 6-15)

All the tested borides corroded heavily under the tested conditions.

III. PREPARATION OF HIGHLY DISPERSED CATALYSTS

A. Noble Metal Alloys (according to E. L. Holt, Nature, 203, 857 (1964))

3.78 gr of Pd-60 Au-alloy have been prepared by reduction with sodium borohydride. B.E.T. measurements show 25.3 m^2/g. In addition, 3.14 gr of Pt-60 Au-alloy with B.E.T. surface of 26.9 m^2/g were prepared using the same method. These materials will be fabricated into electrodes and tested in the floating electrode system. Attempts to precipitate these alloys by reduction with citrate were not successful.

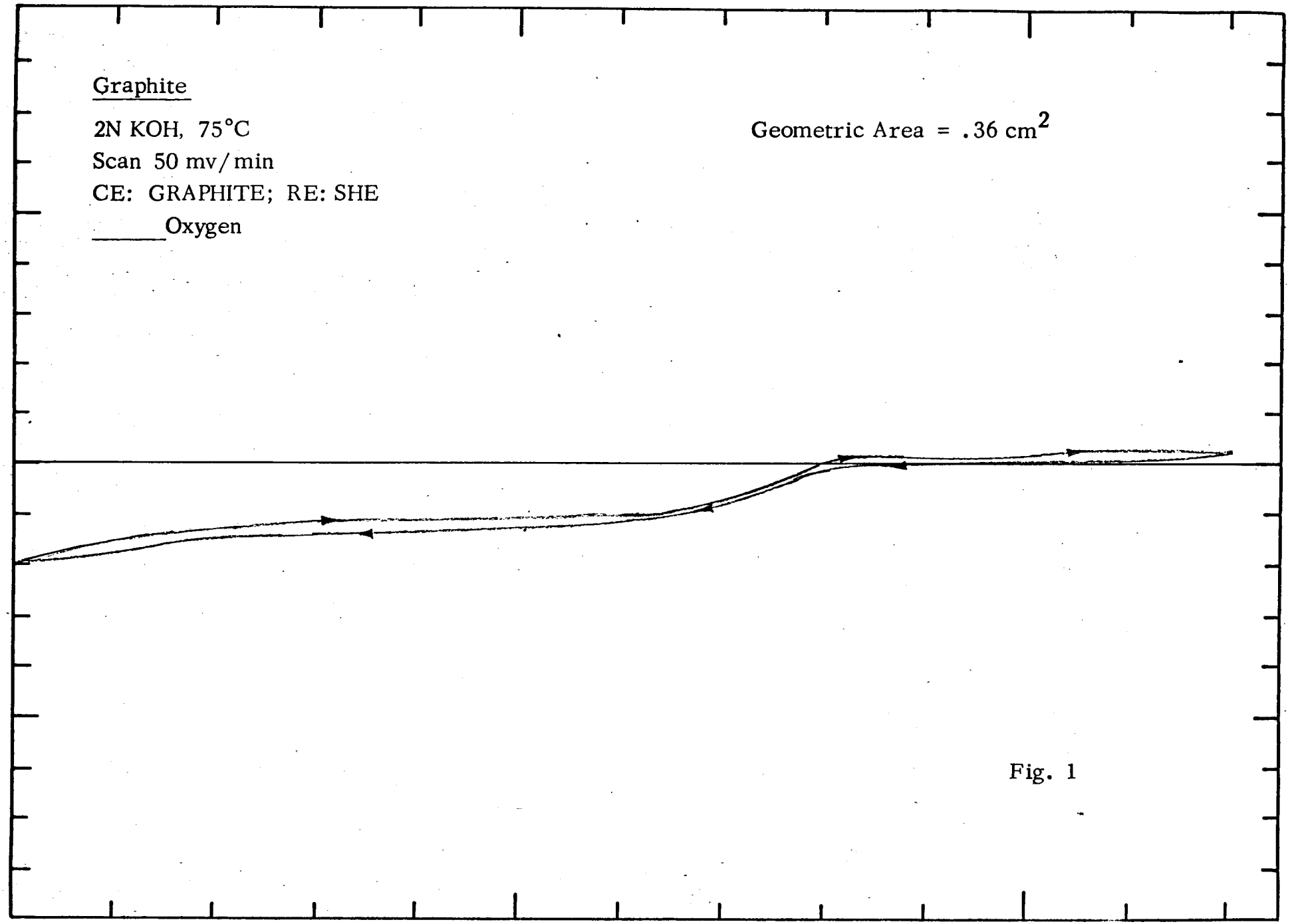
Graphite
2N KOH, 75°C
Scan 50 mv/min
CE: GRAPHITE; RE: SHE
Oxygen
Geometric Area = .36 cm2
.50 v
Potential vs. SHE
1.0v

Fig. 1

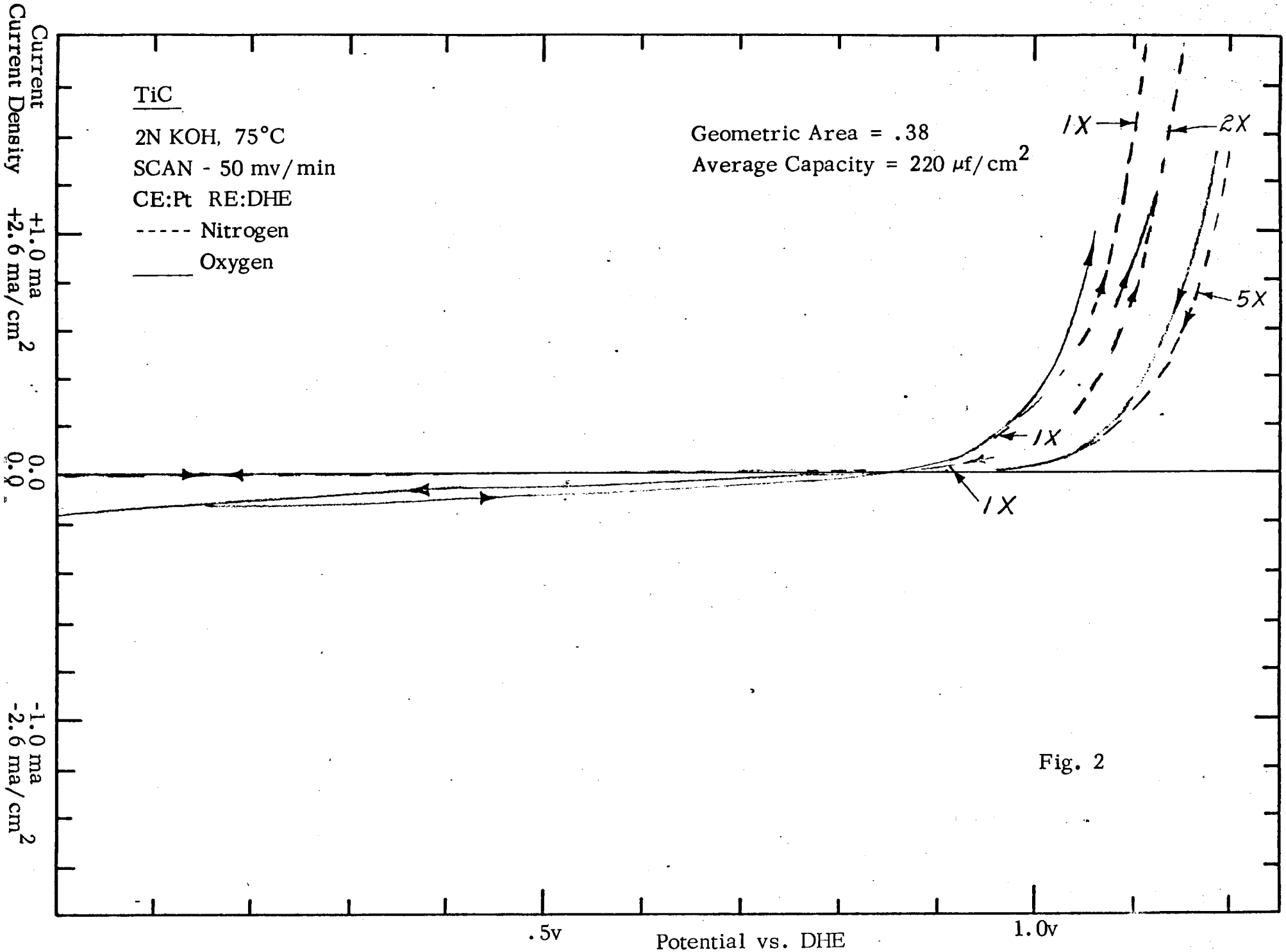
TiC
2N KOH, 75°C
SCAN - 50 mv/min
CE:Pt RE:DHE
----- Nitrogen
_____ Oxygen
Geometric Area = .38
Average Capacity = 220 μf/cm²
1X
2X
5X
1X
1X
Current
Current Density
+1.0 ma
+2.6 ma/cm²
0.0
0.0
-1.0 ma
-2.6 ma/cm²
.5v
1.0v
Potential vs. DHE

Fig. 2

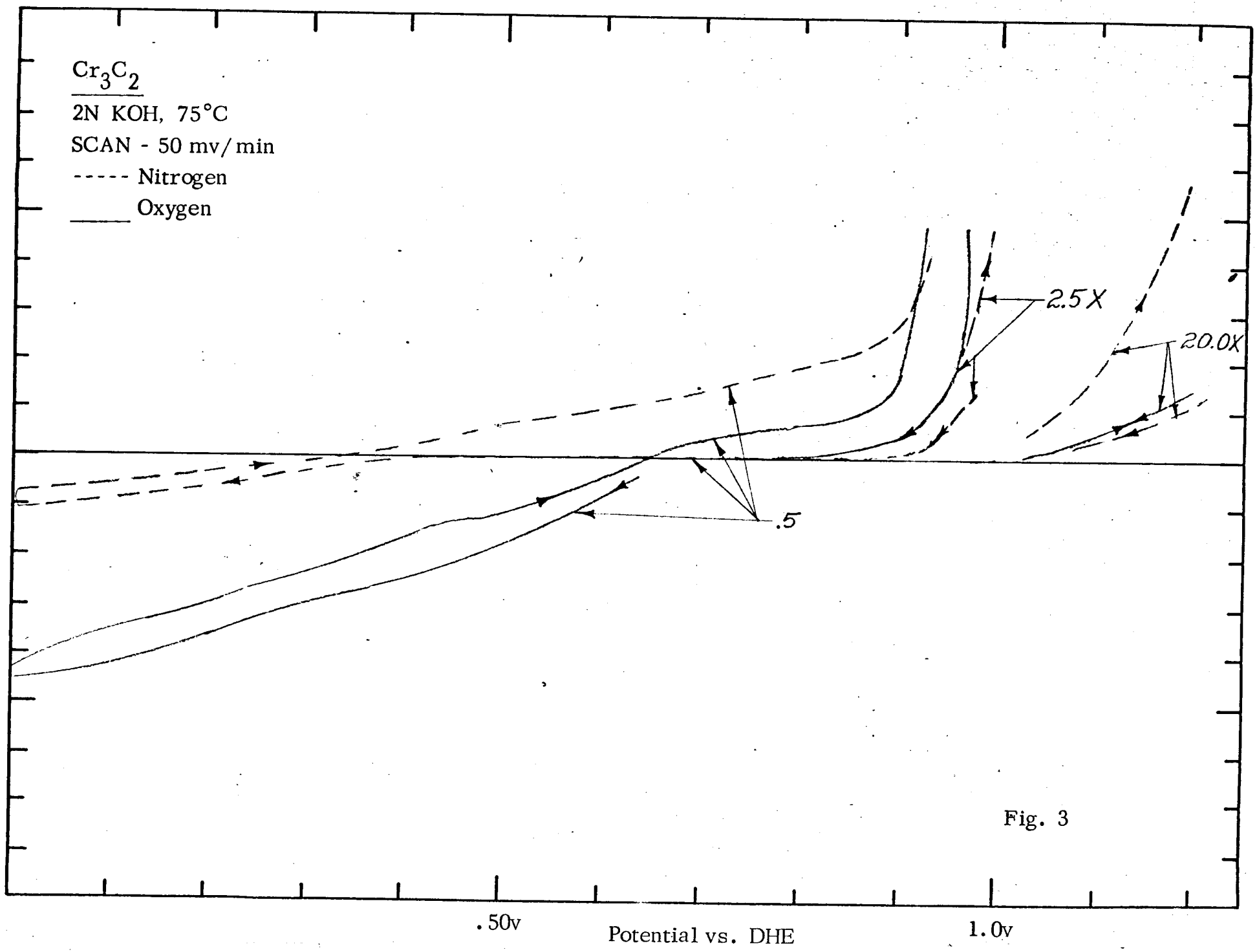
Current
+1.0 ma
0.0
-1.0 ma
Cr_3C_2
2N KOH, 75°C
SCAN - 50 mv/min
----- Nitrogen
_____ Oxygen
2.5X
20.0X
.5
.50v
Potential vs. DHE
1.0v

Fig. 3

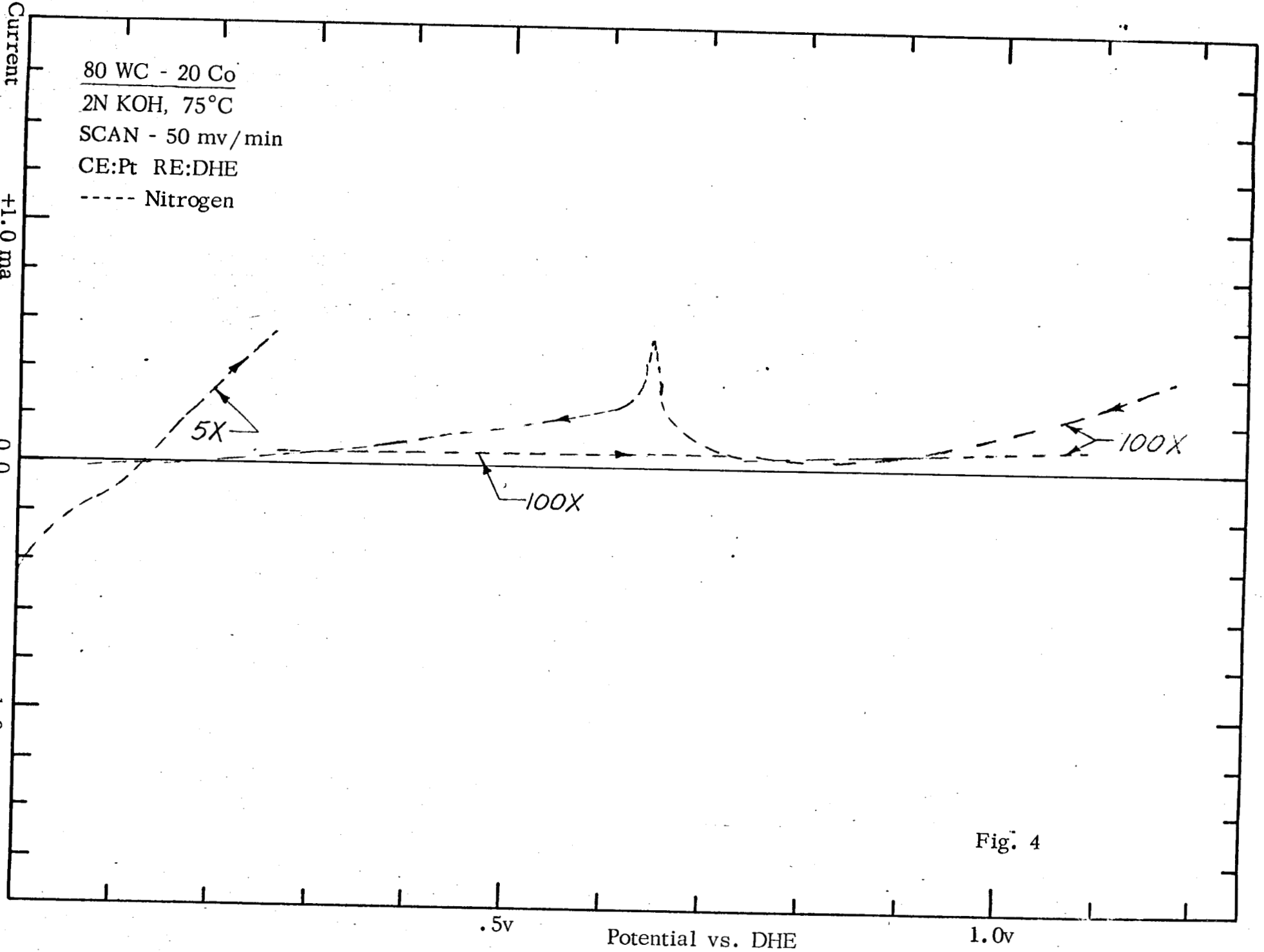
80 WC - 20 Co
2N KOH, 75°C
SCAN - 50 mv/min
CE:Pt RE:DHE
----- Nitrogen
Current
+1.0 ma
0.0
-1.0 ma
5X
100X
100X
.5v
Potential vs. DHE
1.0v

Fig. 4

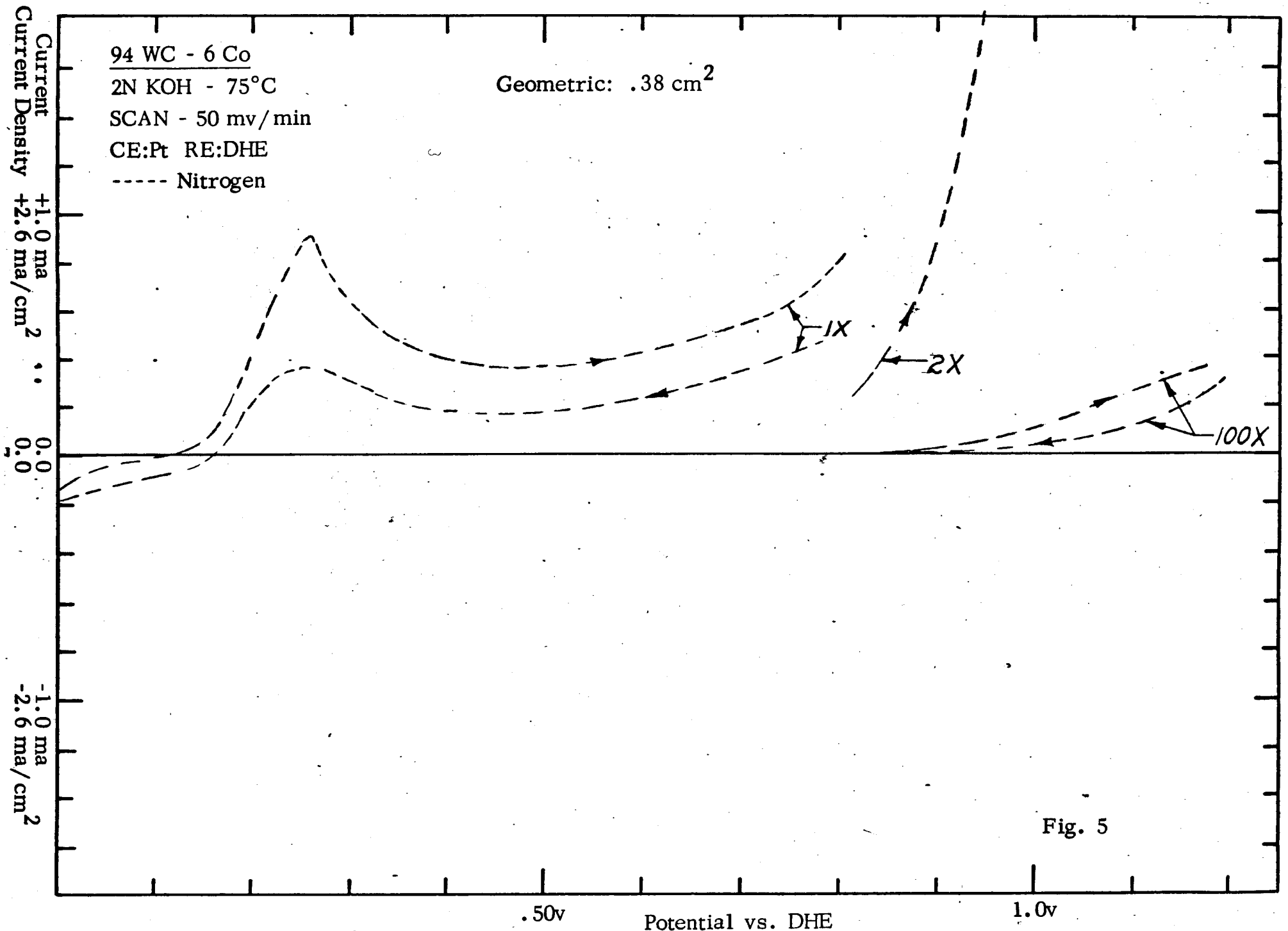
94 WC - 6 Co
2N KOH - 75°C
SCAN - 50 mv/min
CE:Pt RE:DHE
----- Nitrogen
Geometric: .38 cm²
1X
2X
100X
Current
Current Density
+1.0 ma
+2.6 ma/cm²
0.0
0.0
-1.0 ma
-2.6 ma/cm²
.50v
Potential vs. DHE
1.0v

Fig. 5

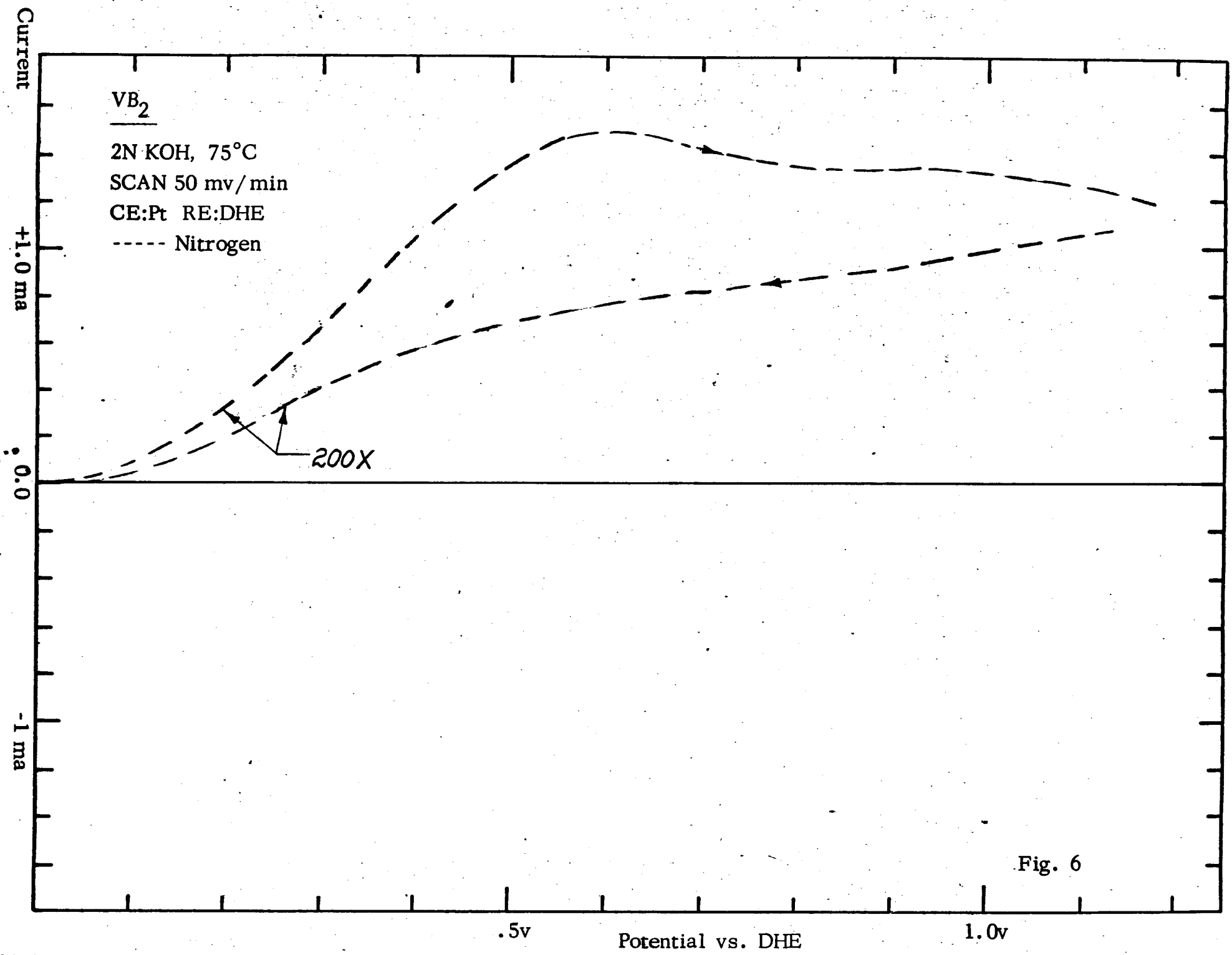
Current
+1.0 ma
0.0
-1 ma
VB2
2N KOH, 75°C
SCAN 50 mv/min
CE:Pt RE:DHE
----- Nitrogen
200X
.5v
Potential vs. DHE
1.0v

Fig. 6

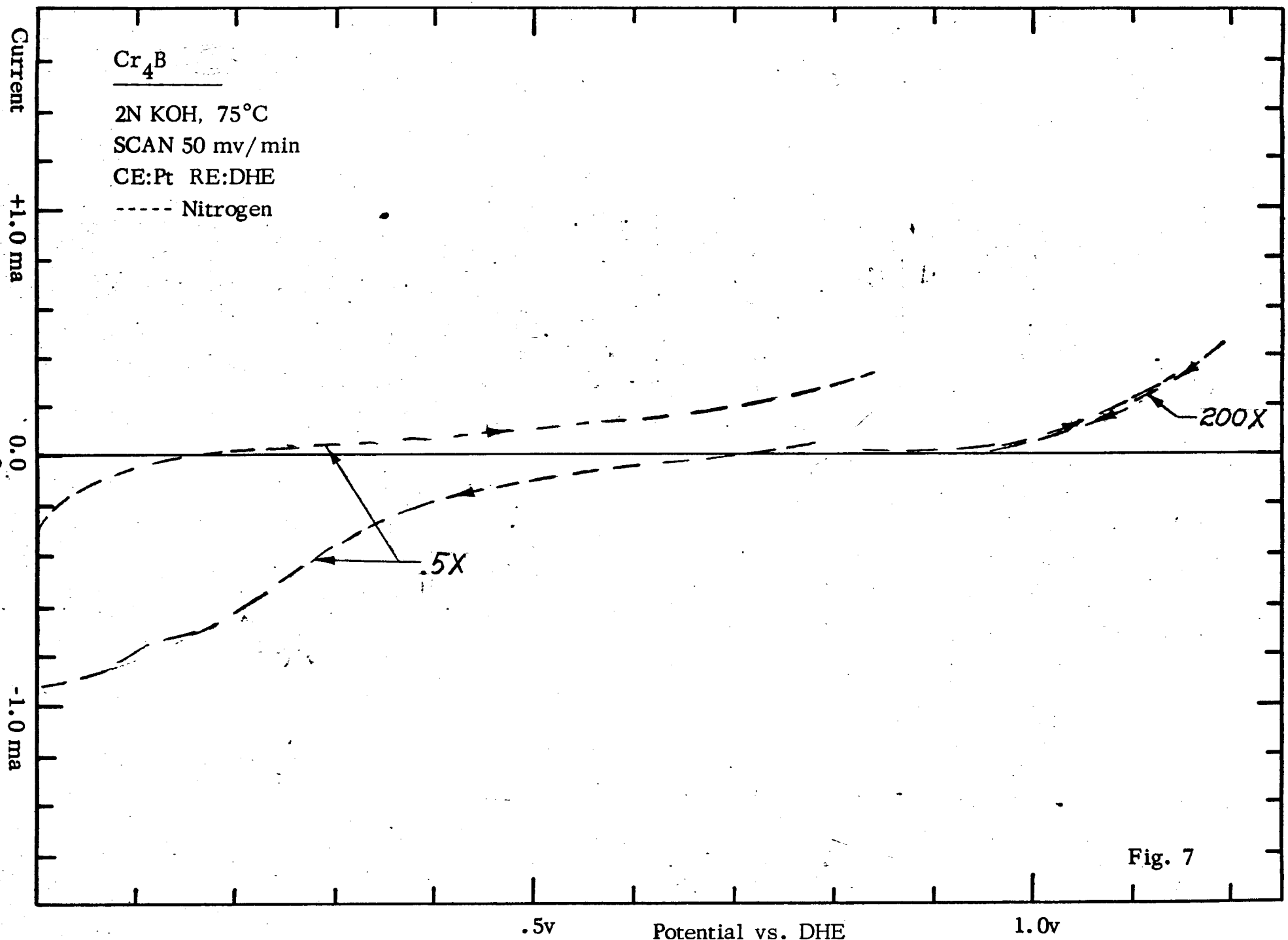
Cr_4B
2N KOH, 75°C
SCAN 50 mv/min
CE:Pt RE:DHE
----- Nitrogen
Current
+1.0 ma
0.0
-1.0 ma
200X
.5X
.5v
Potential vs. DHE
1.0v

Fig. 7

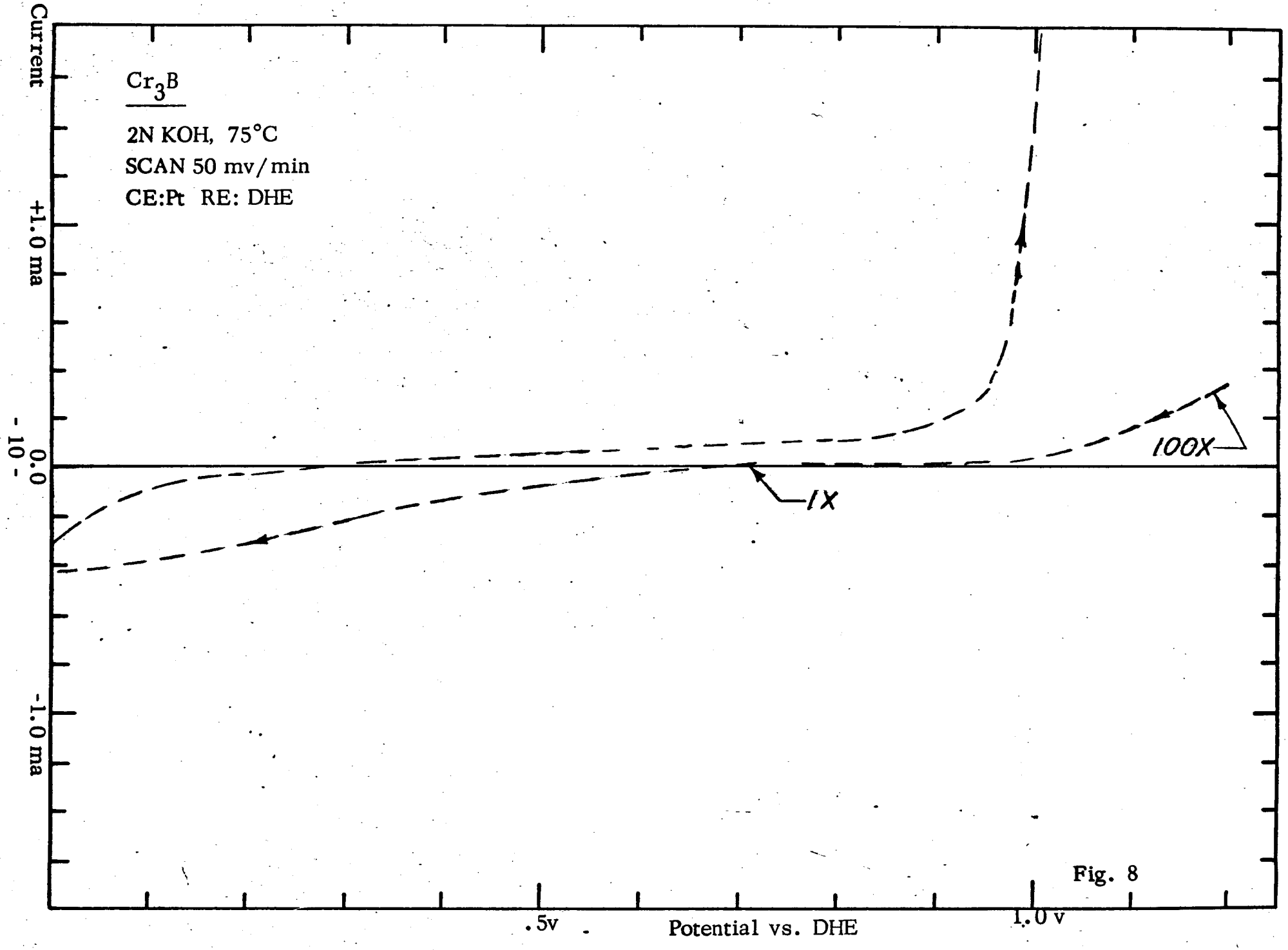
Current
+1.0 ma
0.0
- 10 -
-1.0 ma
Cr_3B
2N KOH, 75°C
SCAN 50 mv/min
CE:Pt RE: DHE
100X
1X
.5v
Potential vs. DHE
1.0 v

Fig. 8

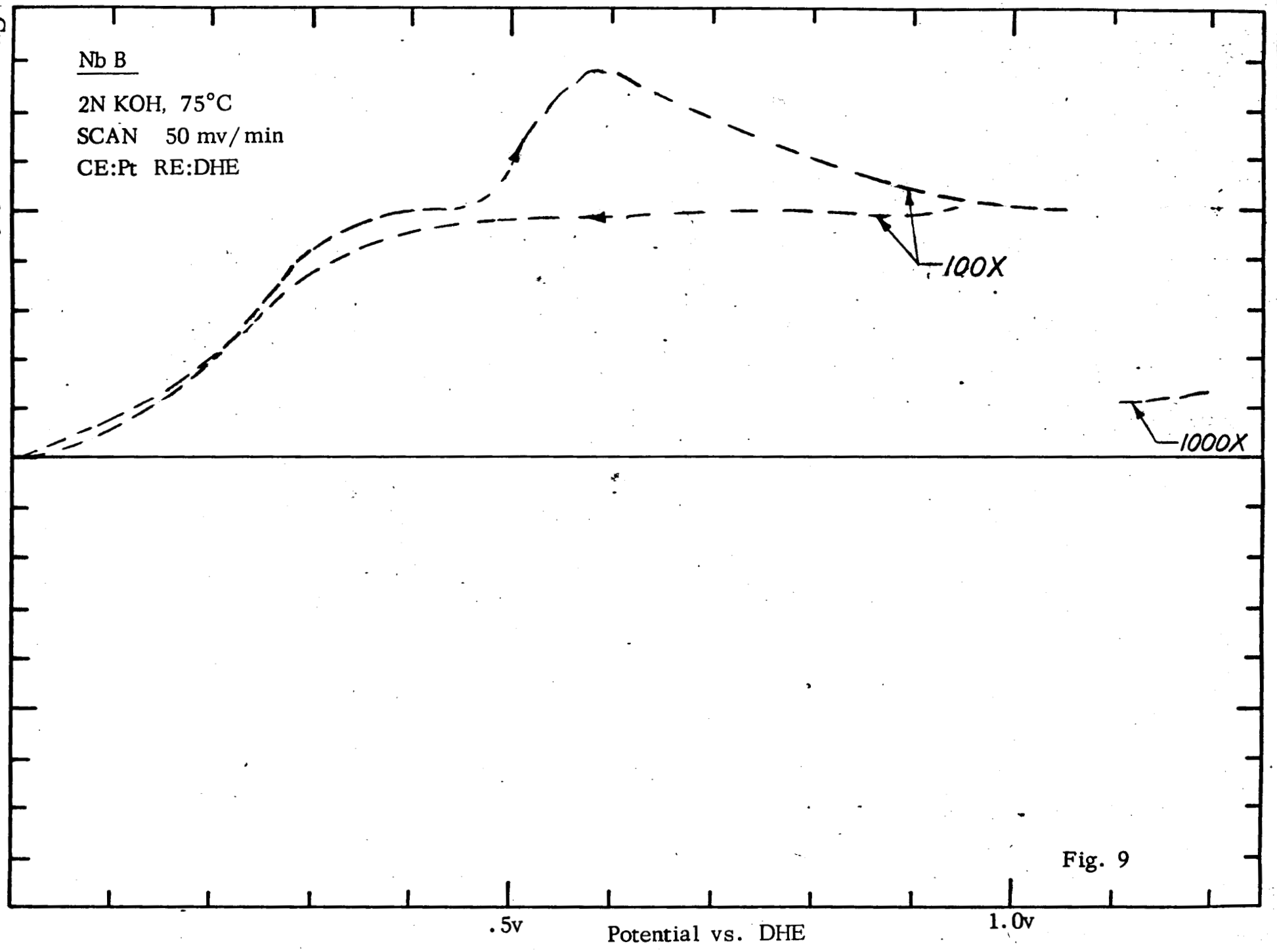
Nb B
2N KOH, 75°C
SCAN 50 mv/min
CE:Pt RE:DHE
Current
+1.0 ma
0.0
-1.0 ma
100X
1000X
.5v
1.0v
Potential vs. DHE

Fig. 9

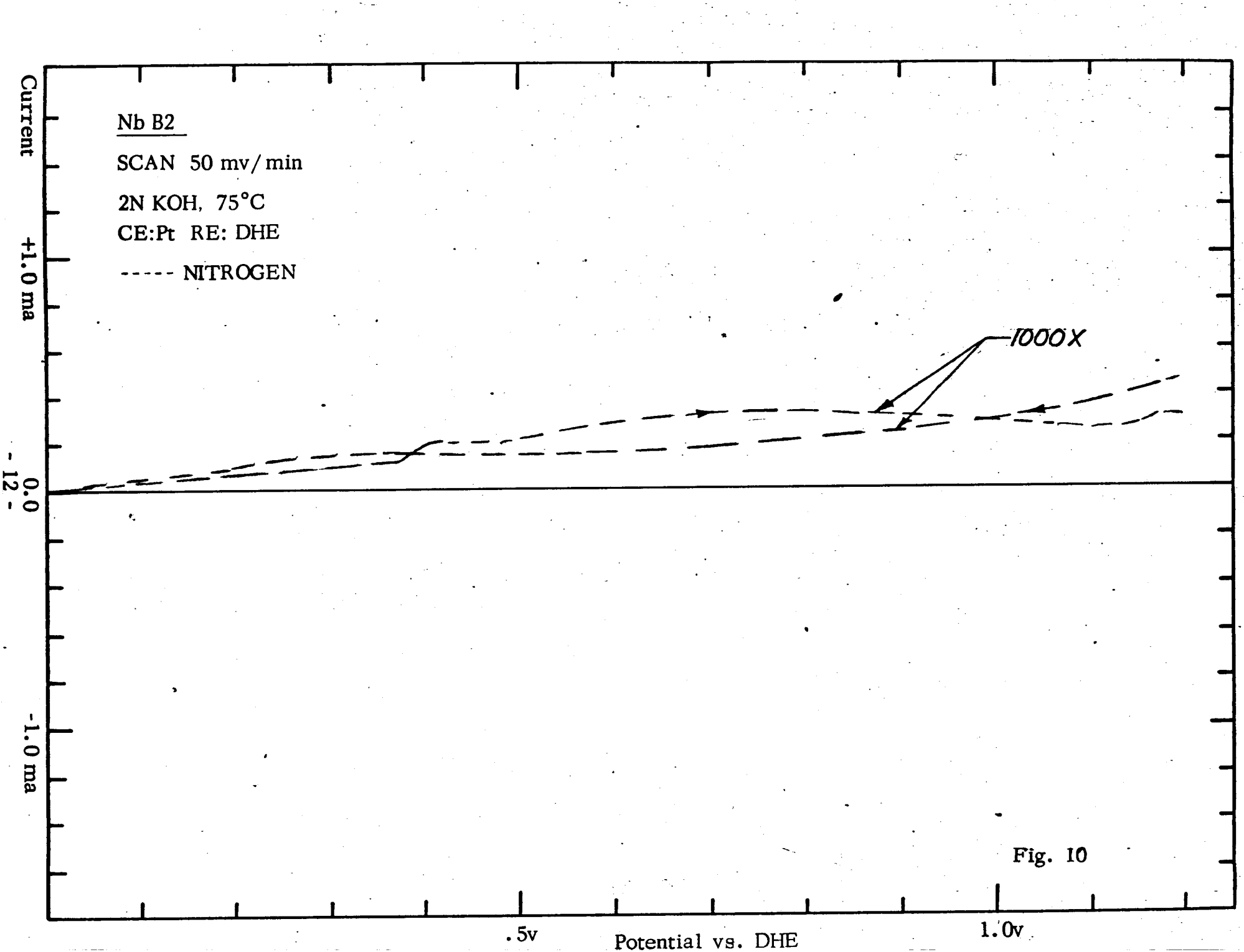
Current
+1.0 ma
0.0
- 12 -
-1.0 ma
Nb B2
SCAN 50 mv/min
2N KOH, 75°C
CE:Pt RE: DHE
----- NITROGEN
1000X
.5v
Potential vs. DHE
1.0v

Fig. 10

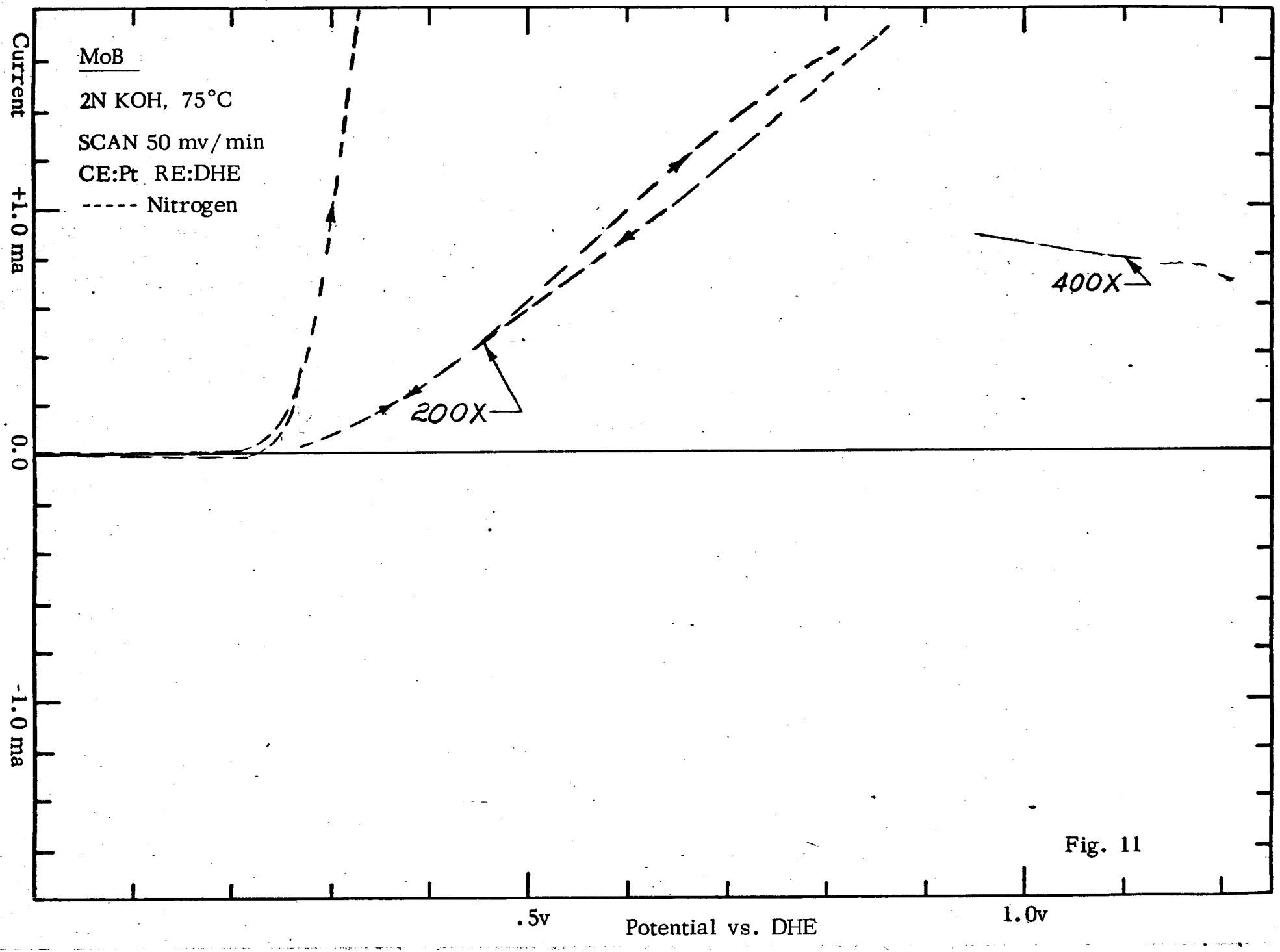
MoB
2N KOH, 75°C
SCAN 50 mv/min
CE:Pt RE:DHE
----- Nitrogen
Current
+1.0 ma
0.0
-1.0 ma
200X
400X
.5v
1.0v
Potential vs. DHE

Fig. 11

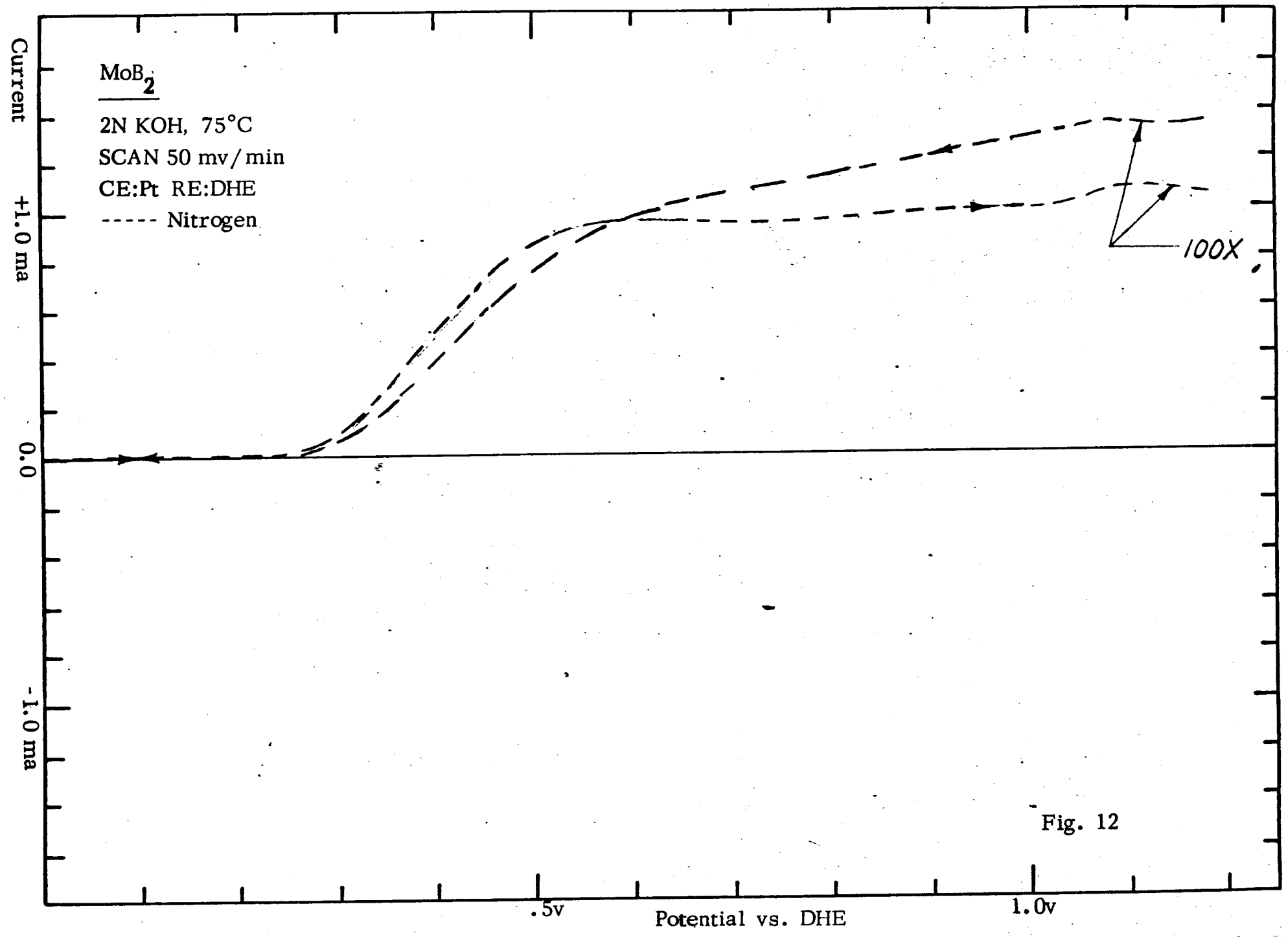
MoB2
2N KOH, 75°C
SCAN 50 mv/min
CE:Pt RE:DHE
----- Nitrogen
100X
Current
+1.0 ma
0.0
-1.0 ma
.5v
1.0v
Potential vs. DHE

Fig. 12

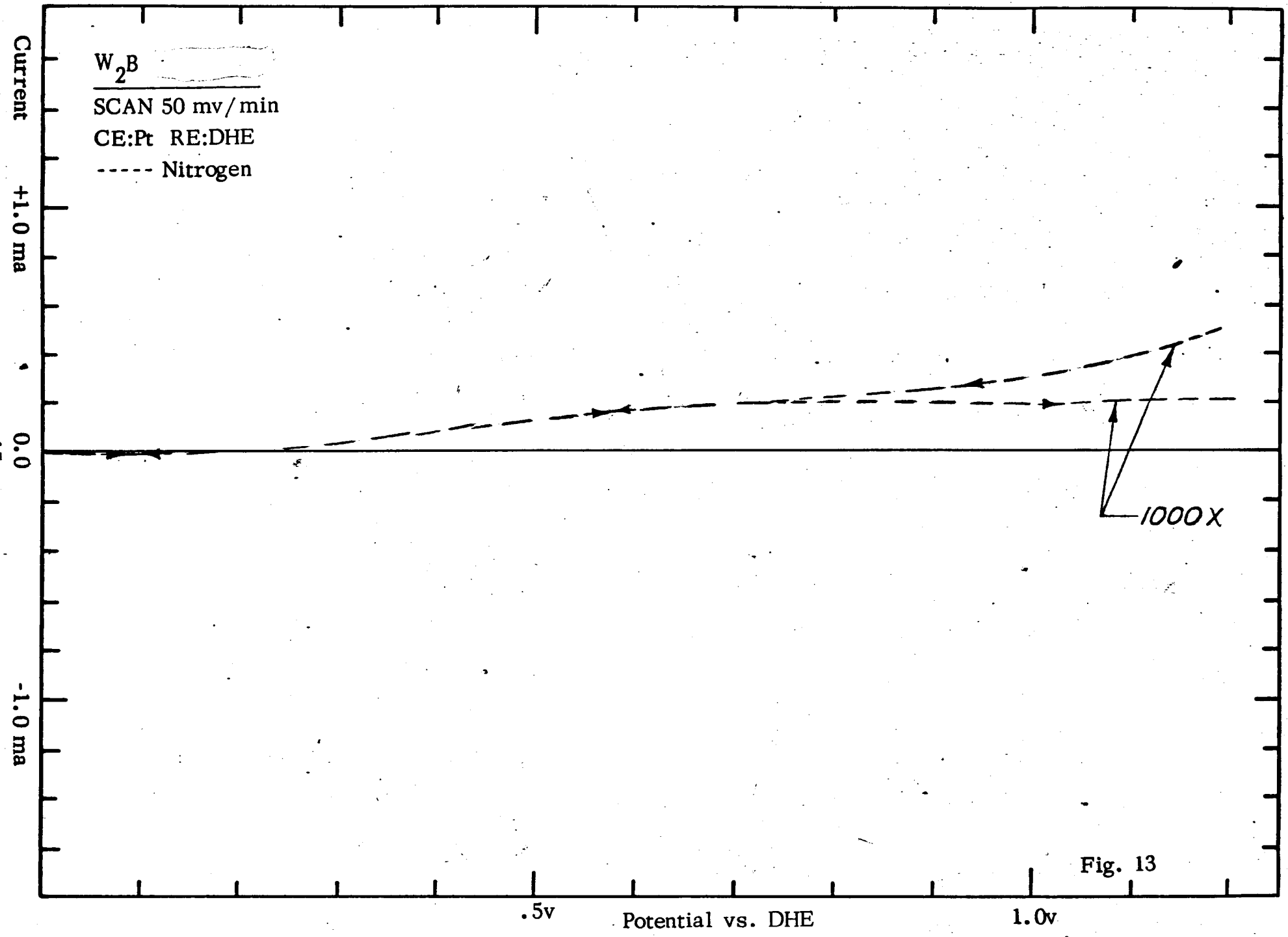
W_2B
SCAN 50 mv/min
CE:Pt RE:DHE
----- Nitrogen
Current
+1.0 ma
0.0
-1.0 ma
1000X
.5v
Potential vs. DHE
1.0v

Fig. 13

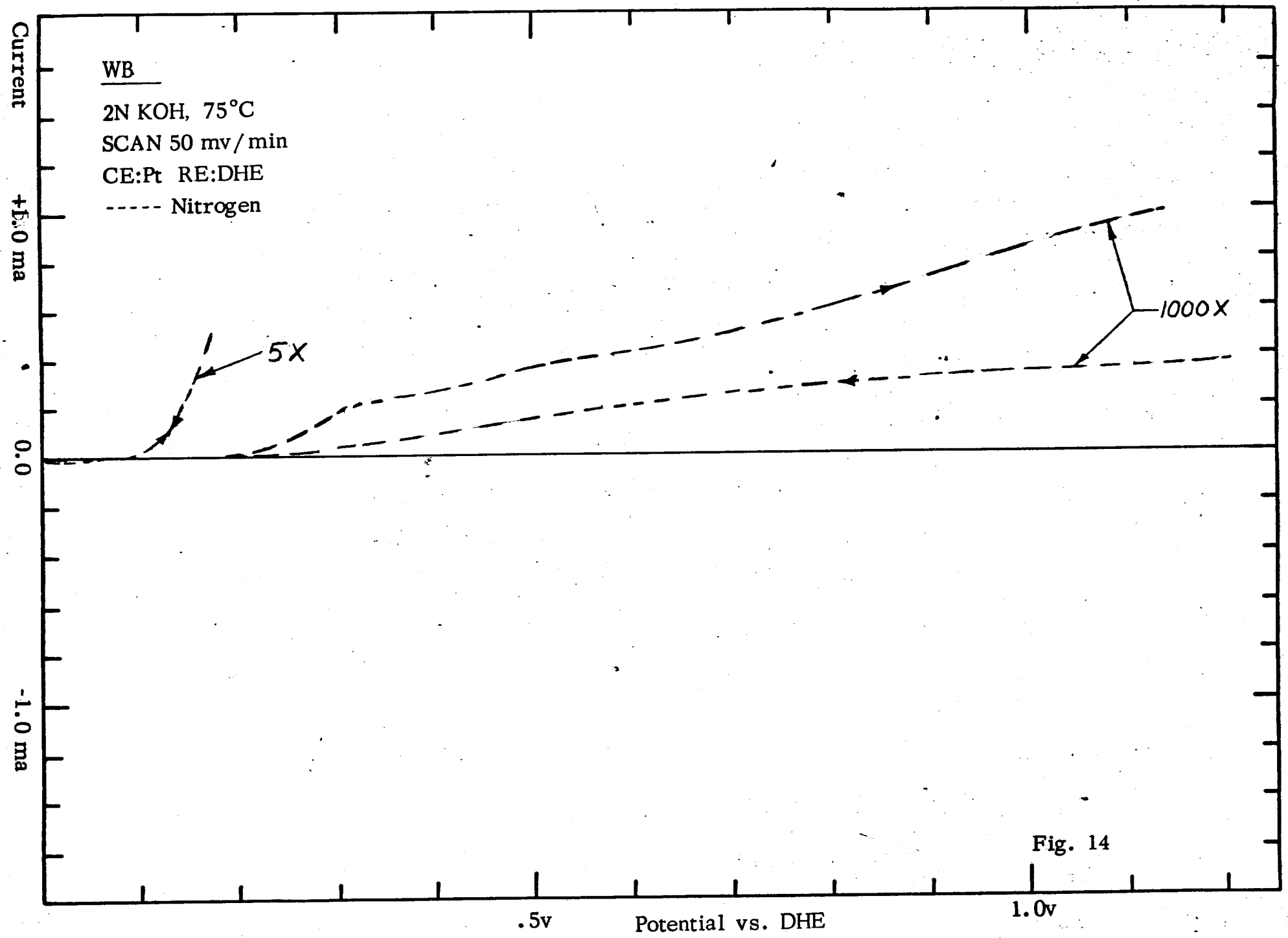
WB
2N KOH, 75°C
SCAN 50 mv/min
CE:Pt RE:DHE
----- Nitrogen
5X
1000X
Current
+1.0 ma
0.0
-1.0 ma
.5v
Potential vs. DHE
1.0v

Fig. 14

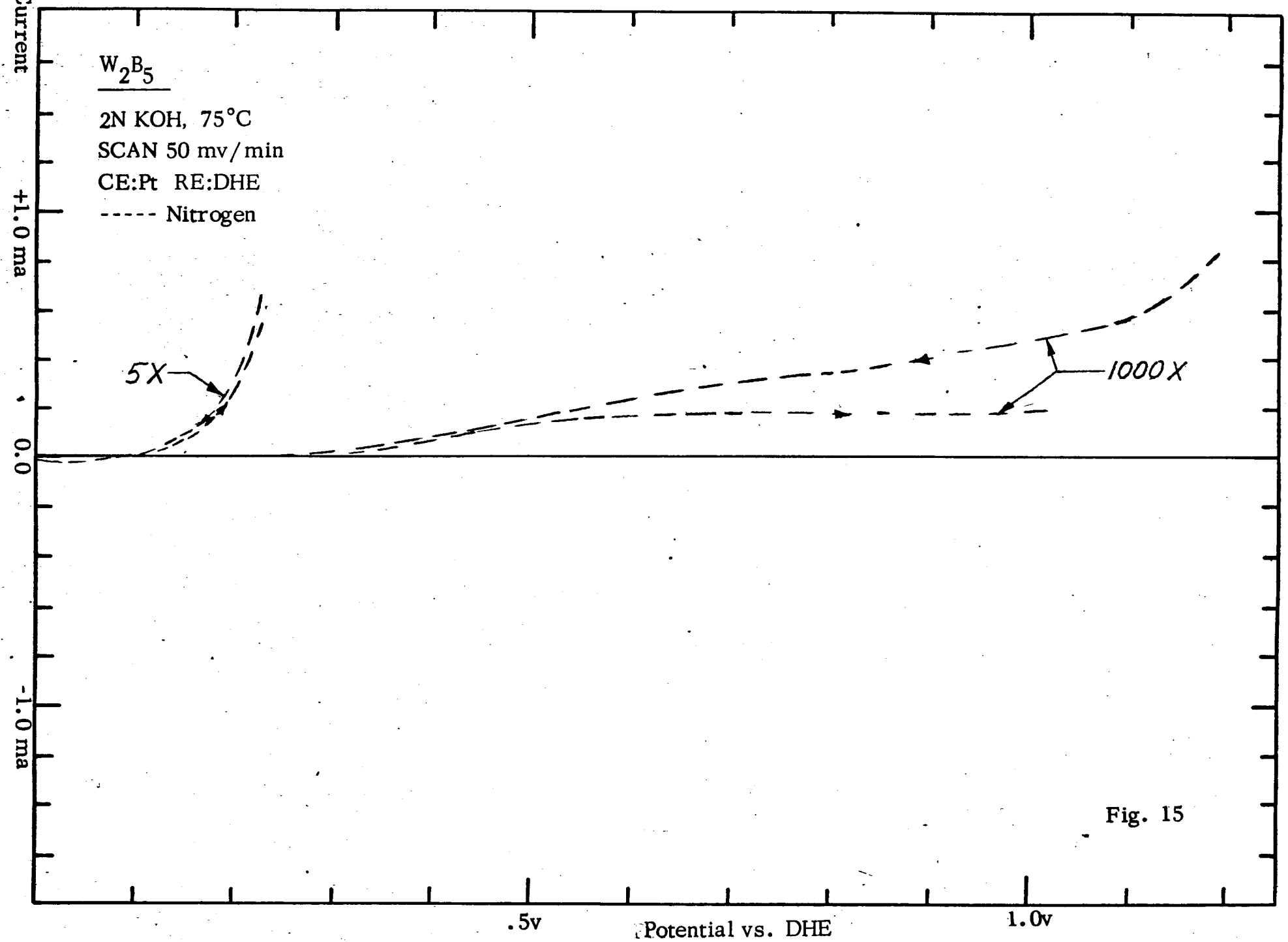
W_2B_5
2N KOH, 75°C
SCAN 50 mv/min
CE:Pt RE:DHE
----- Nitrogen
5X
1000X
Current
+1.0 ma
0.0
-1.0 ma
.5v
1.0v
Potential vs. DHE

Fig. 15

B. Preparation of Cementite from Fe-salt of Mellitic Acid (according to Freel and Galwey, Nature, 208, 183 (1965))

The material obtained by this technique was highly pyrophonic. We are attempting to reduce the surface area (which now is probably higher than 200 m^2/g) by decreasing the decomposition temperature. Another possibility which we plan to test is the slow oxidation, either by successive change of solvents or by oxidation at controlled oxygen partial pressure.

C. Carburization of Fe-sponge

Fe-sponge, 99.999% pure with a B.E.T. area of 0.5 m^2/g was reduced under H_2 at 350°C for 28 hrs. Afterwards it was carburized at 200°C for 24 hrs and at 250°C for 8 hrs. X-ray diffraction patterns show a mixture of Fe_2C and Fe_3C with no iron oxide or iron. This sample has been used to make an electrode which was tested as a floating electrode (Fig. 27).

Treatment of this material at 475°C under N_2 for 4 hours rendered a material with diffraction patterns of cementite.

At the present moment Ni_3C and Fe_2C (both as a highly dispersed product and as surface layer on compact metal) are being prepared.

IV. FLOATING ELECTRODE MEASUREMENTS

Several measurements with commercial platinum-Teflon pasted screen electrodes have been done to calibrate the floating electrode cell. Potentiostatic i (E)-curves were obtained at 75°C in 35% KOH. The current was recorded for 5 min at 50 mv intervals. The potential was maintained vs. the dynamic hydrogen electrode which was calibrated against the floating electrode in hydrogen atmosphere at open circuit. A correction of - 30 mv has been found necessary, and has been already introduced in the curves of Figs. 18-27.

The iR drop between the floating electrode and the tip of the Haber-Luggin capillary was determined using the interruptor technique. A fast interruption was achieved using a mercury relay switch. The potential-decay was recorded with the help of an oscilloscope using fast time scale (0.5 msec/cm). The very abrupt potential drop immediately after current interruption (seen as a discontinuity in the oscilloscope picture) is equal to the iR drop. Sketches of the apparatus are shown in Figs. 16 and 17, and i (E)-curves for O_2 and H_2 (as comparison) obtained with several commercial electrodes are given in Figs. 18-23.

Silver Electrode (Figs. 24-26)

Porous Ag-electrodes have been made by mixing AgO powder and Teflon, spreading the mixture on Ni-screen, and sintering at temperatures between 250°C and 350°C.

In the first sample, a mixture of 20% Teflon, 80% AgO, was sintered at 250°C for 2 min. The i (e)-curve (Fig. 24) shows reasonably good activity for the O_2-reduction, although lower by about 50 mv than the average Pt-Teflon electrode (Figs. 18-20). Reduction of the Teflon content to 15% causes a decay of performance (Fig. 25). Additional performance decay is caused by increasing the sintering temperature to 350°C (Fig. 26).

Fe_2C-Fe_3C (Fig. 27)

Shows the i (E)-curve for an electrode made of Fe_2C-Fe_3C powder mixed with Teflon (to 30%) and sintered at 250°C for 2 min. The measured activity is sizable, but poorer than that of Ag and Pt. Correction of the iR-drop shows very high resistance. This point and the effect of Teflon content are being investigated at the present.

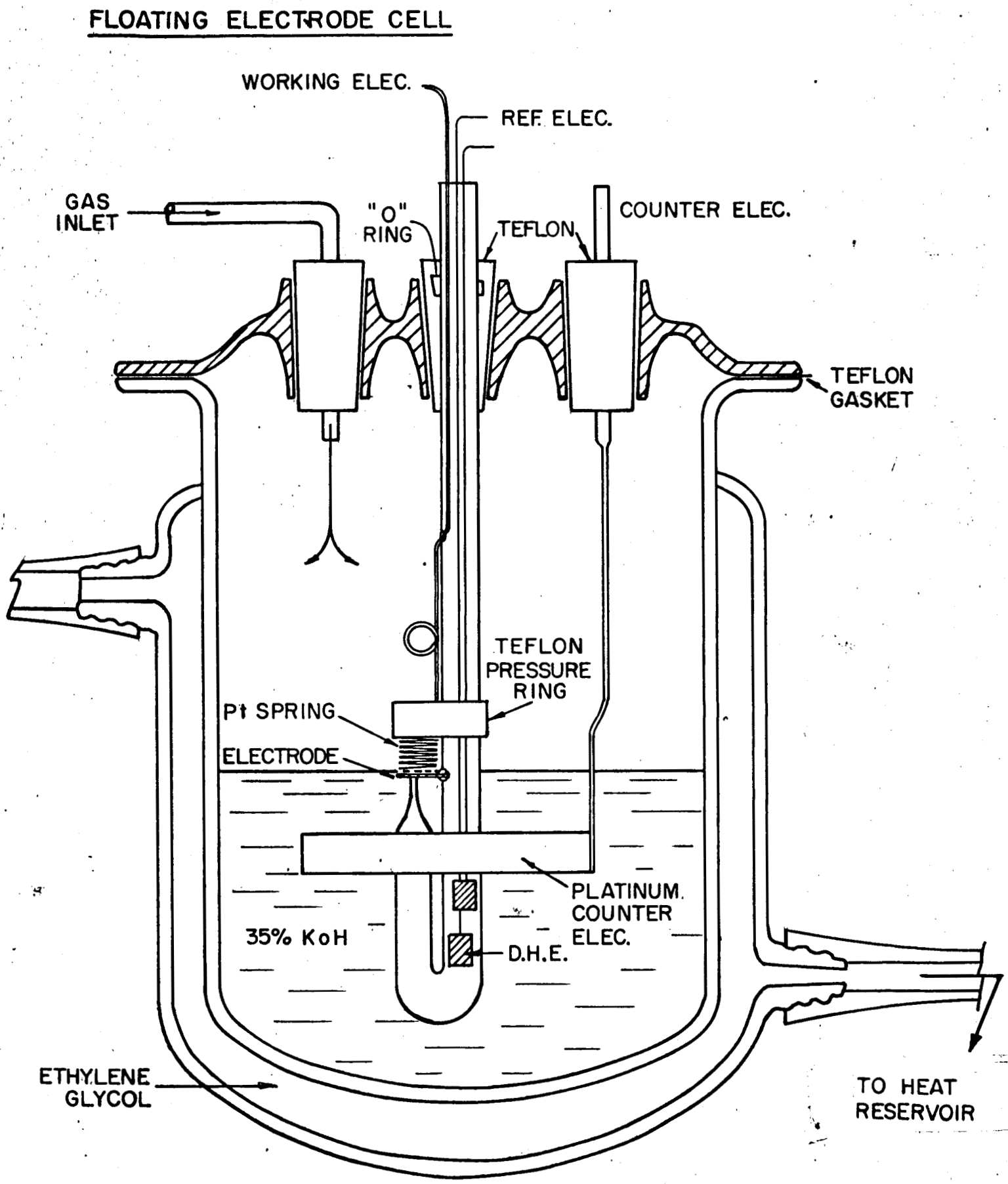

Fig. 16 Floating electrode cell

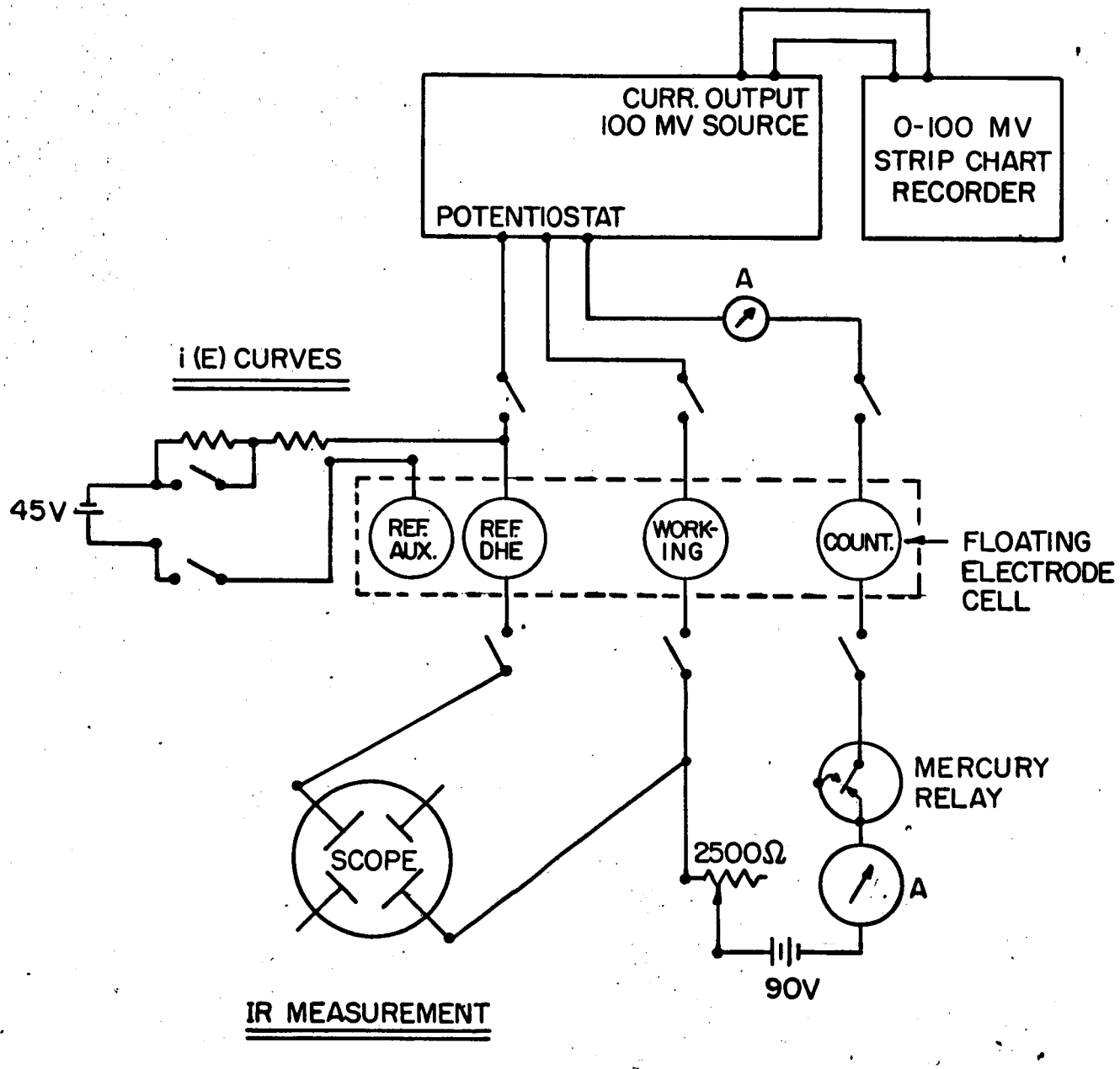

Fig. 17 Floating electrode cell instrumentation for iR determination.

K+E 10 X 10 TO THE CENTIMETER 46 1523
18 X 25 CM. MADE IN U.S.A.
KEUFFEL & ESSER CO.

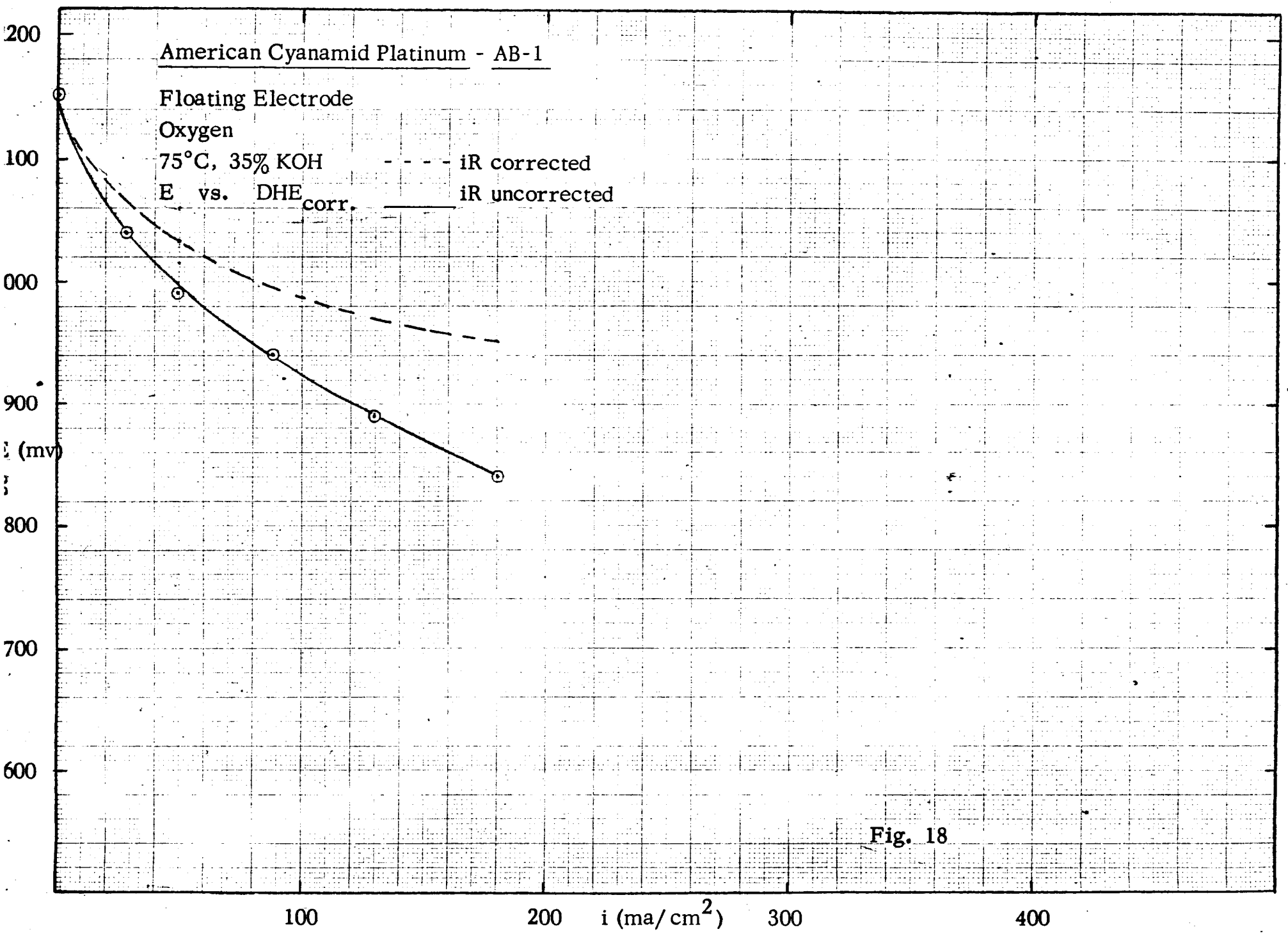

Fig. 18

K+E 10 X 10 TO THE CENTIMETER 46 1523
18 X 25 CM. MADE IN U.S.A.
KEUFFEL & ESSER CO.

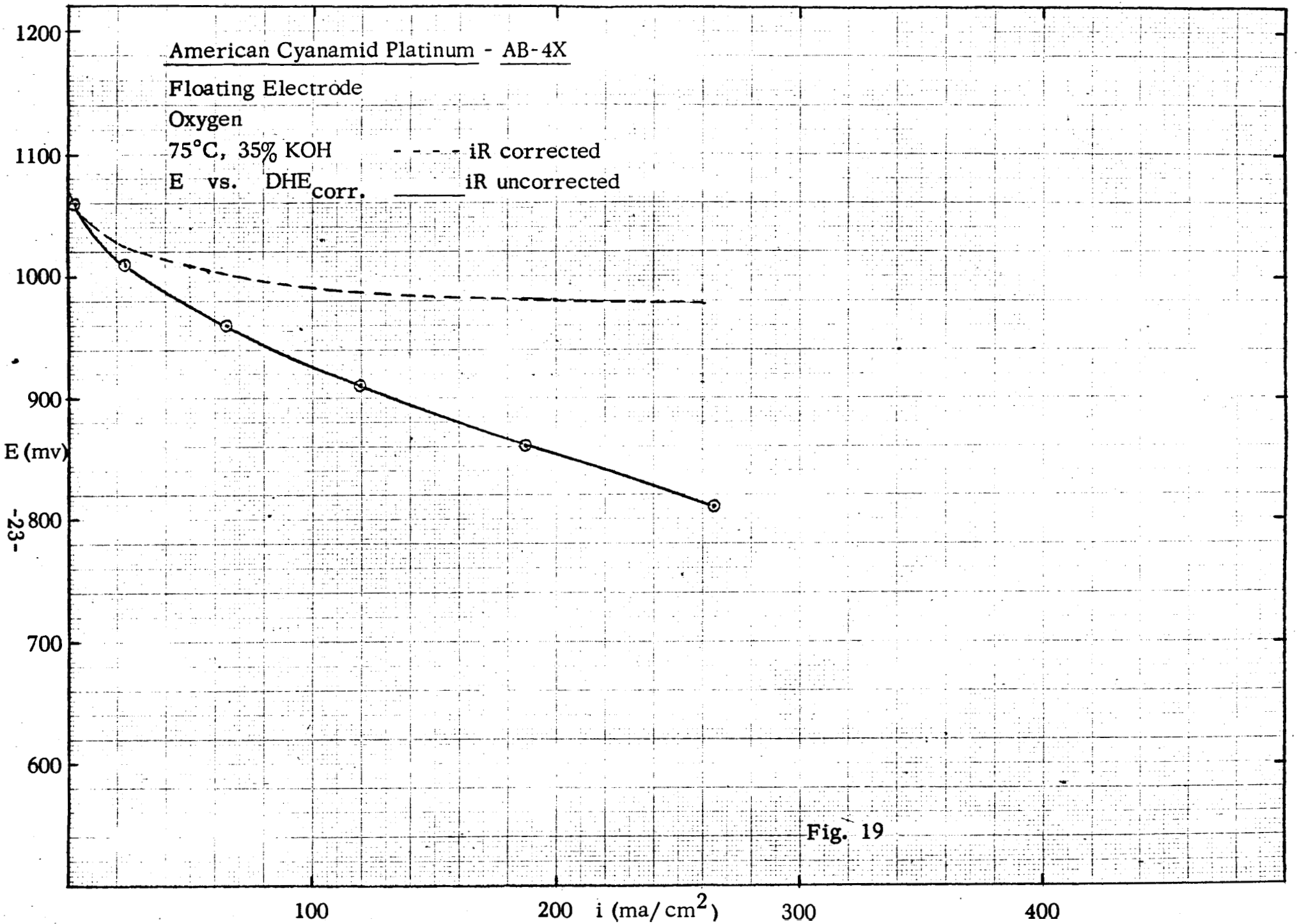

Fig. 19

K+E 10 X 10 TO THE CENTIMETER 46 1523
18 X 25 CM. MADE IN U.S.A.
KEUFFEL & ESSER CO.

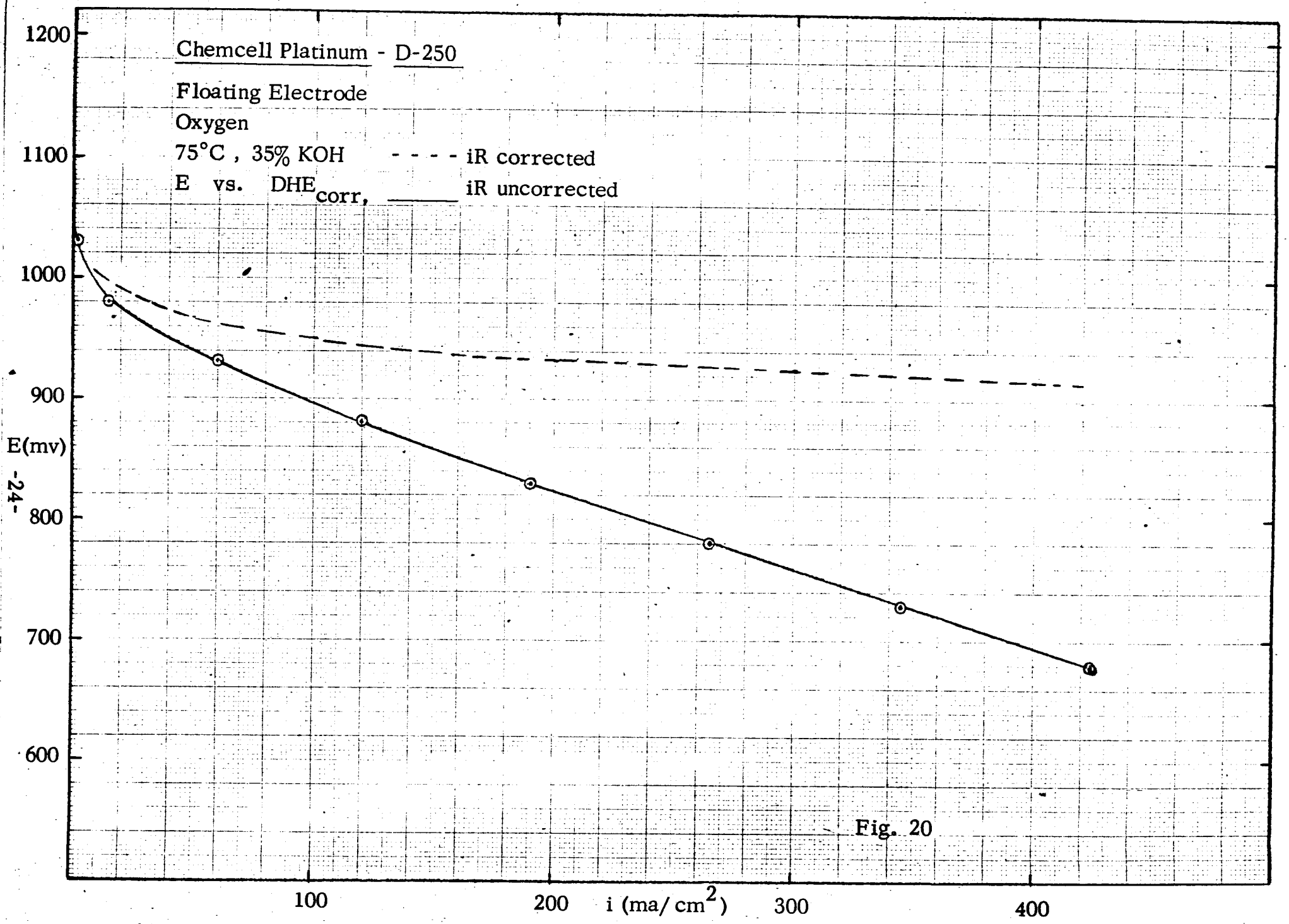

Fig. 20

KEUFFEL & ESSER CO.

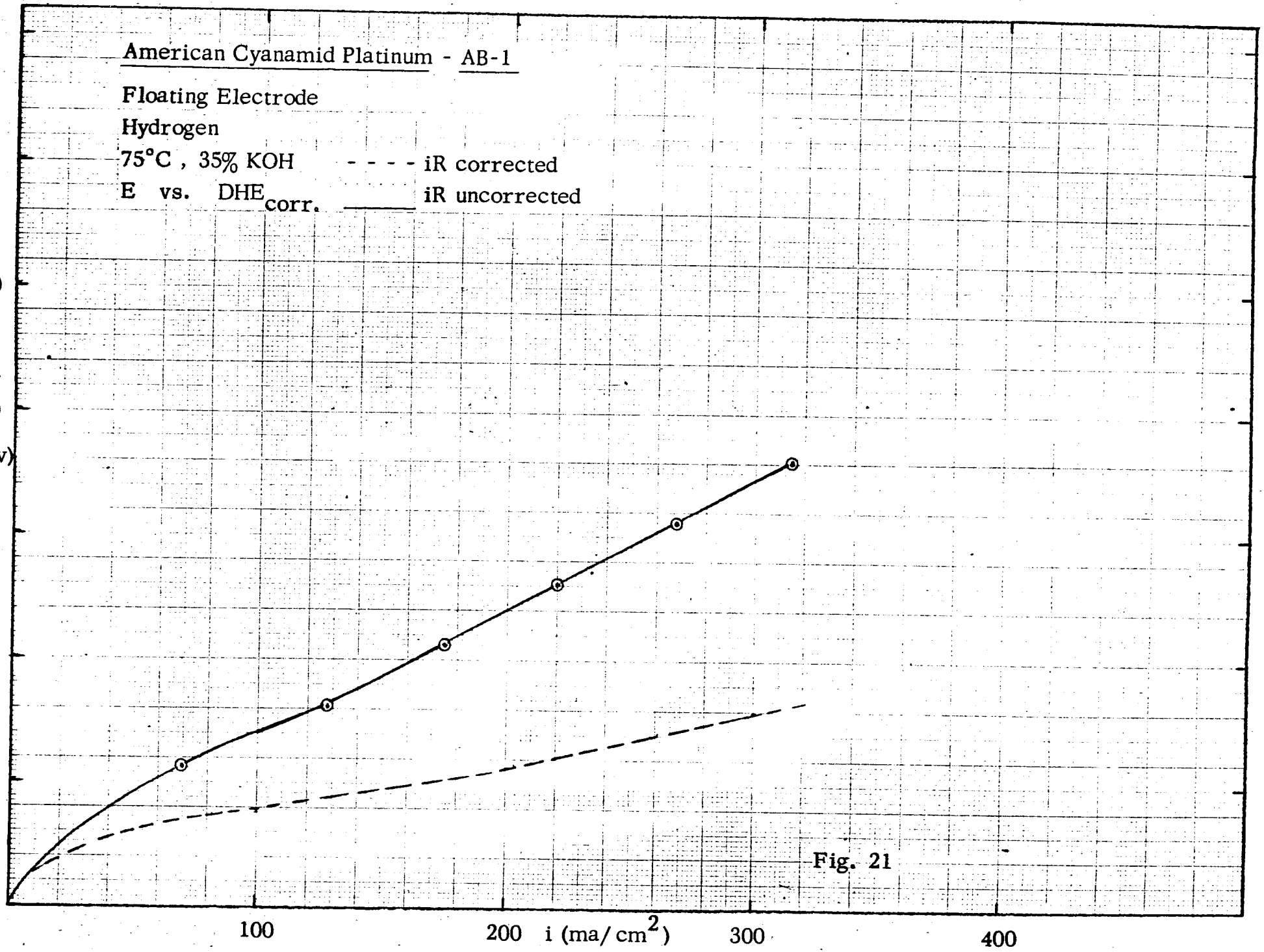

Fig. 21

18 X 25 CM. MADE IN U.S.A.
KEUFFEL & ESSER CO.

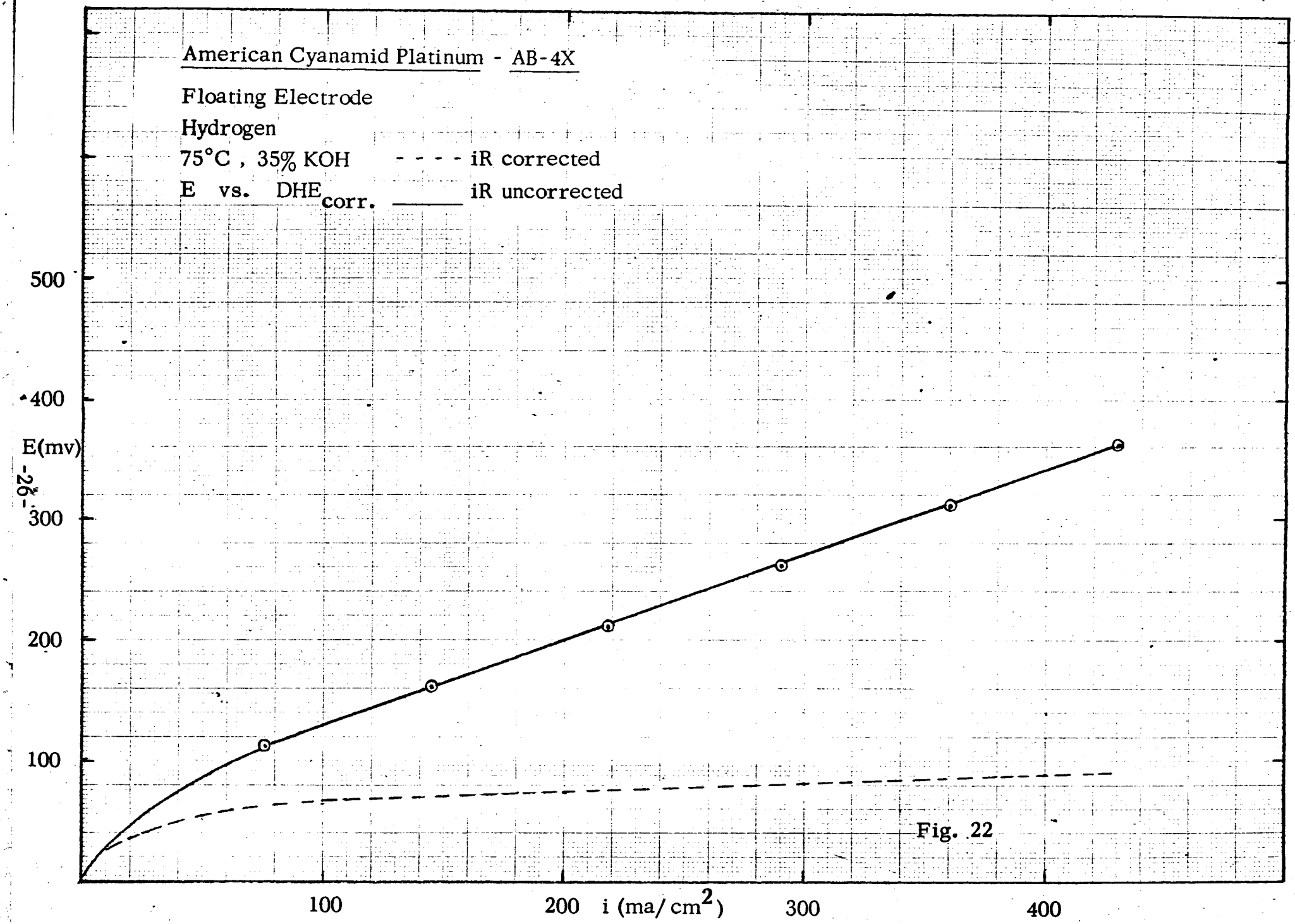

Fig. 22

KEUFFEL & ESSER CO.

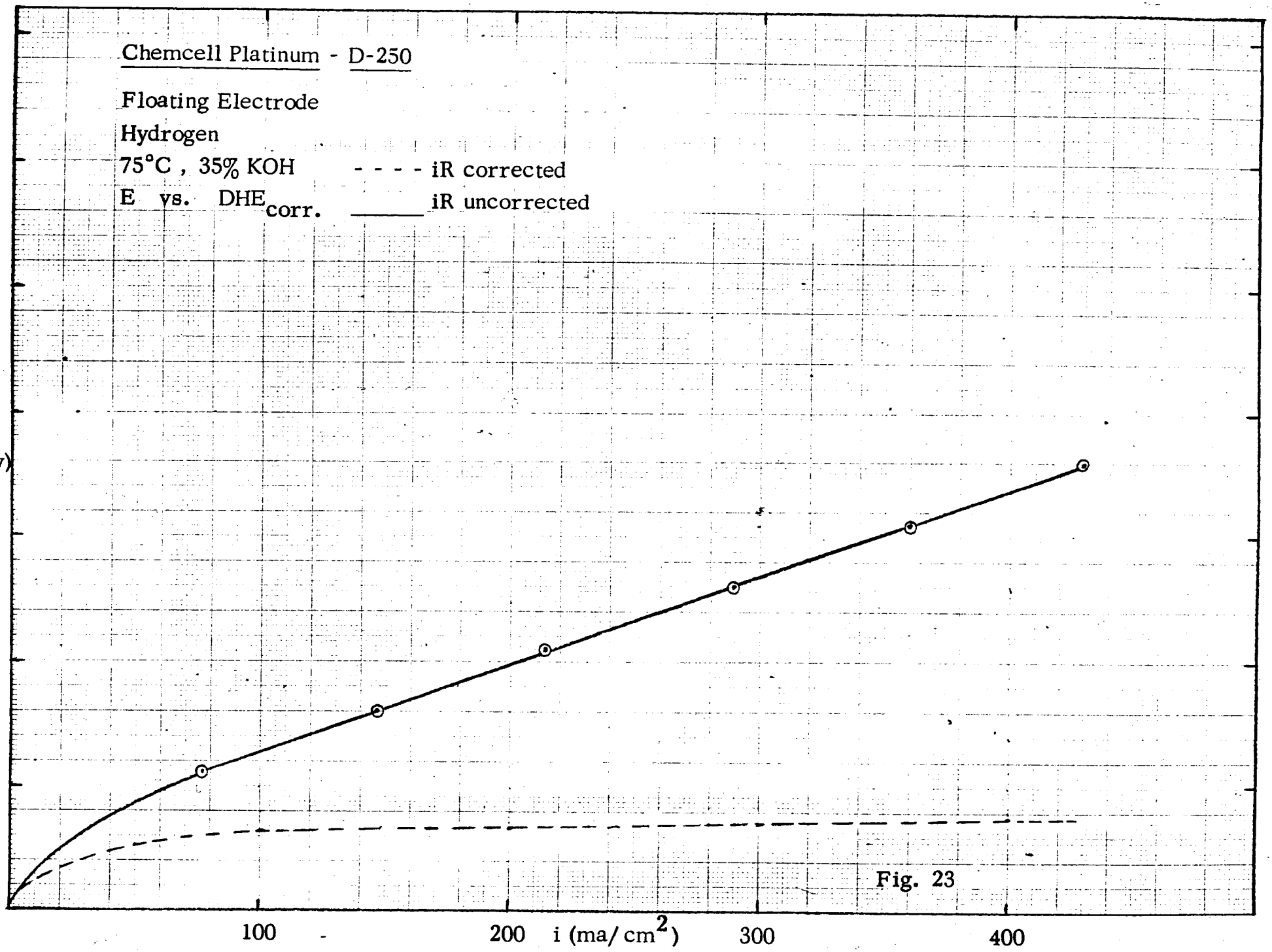

Fig. 23

18 X 25 CM. KEUFFEL & ESSER CO. MADE IN U.S.A.

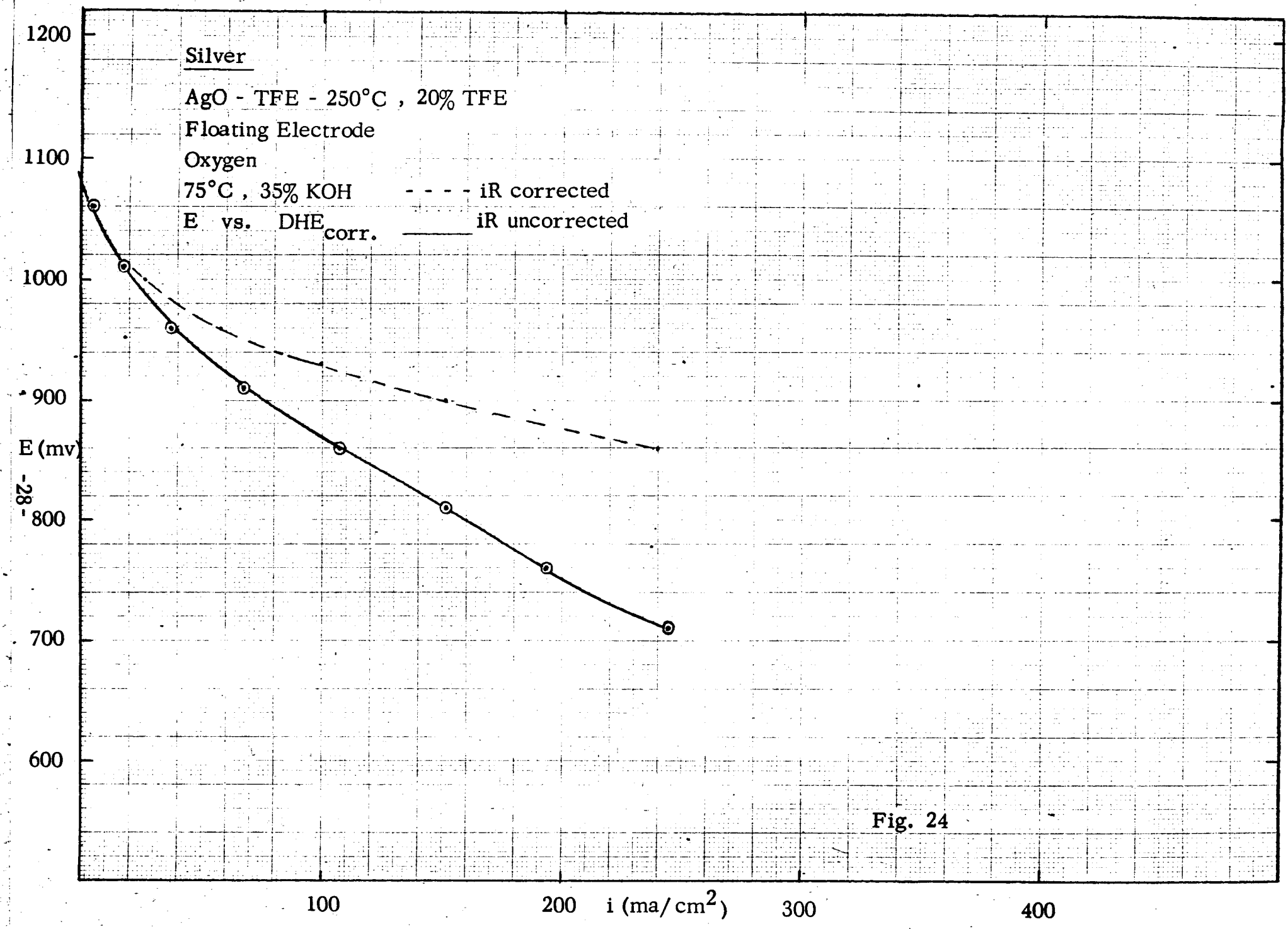

Fig. 24

KEUFFEL & ESSER CO.
MADE IN U.S.A.

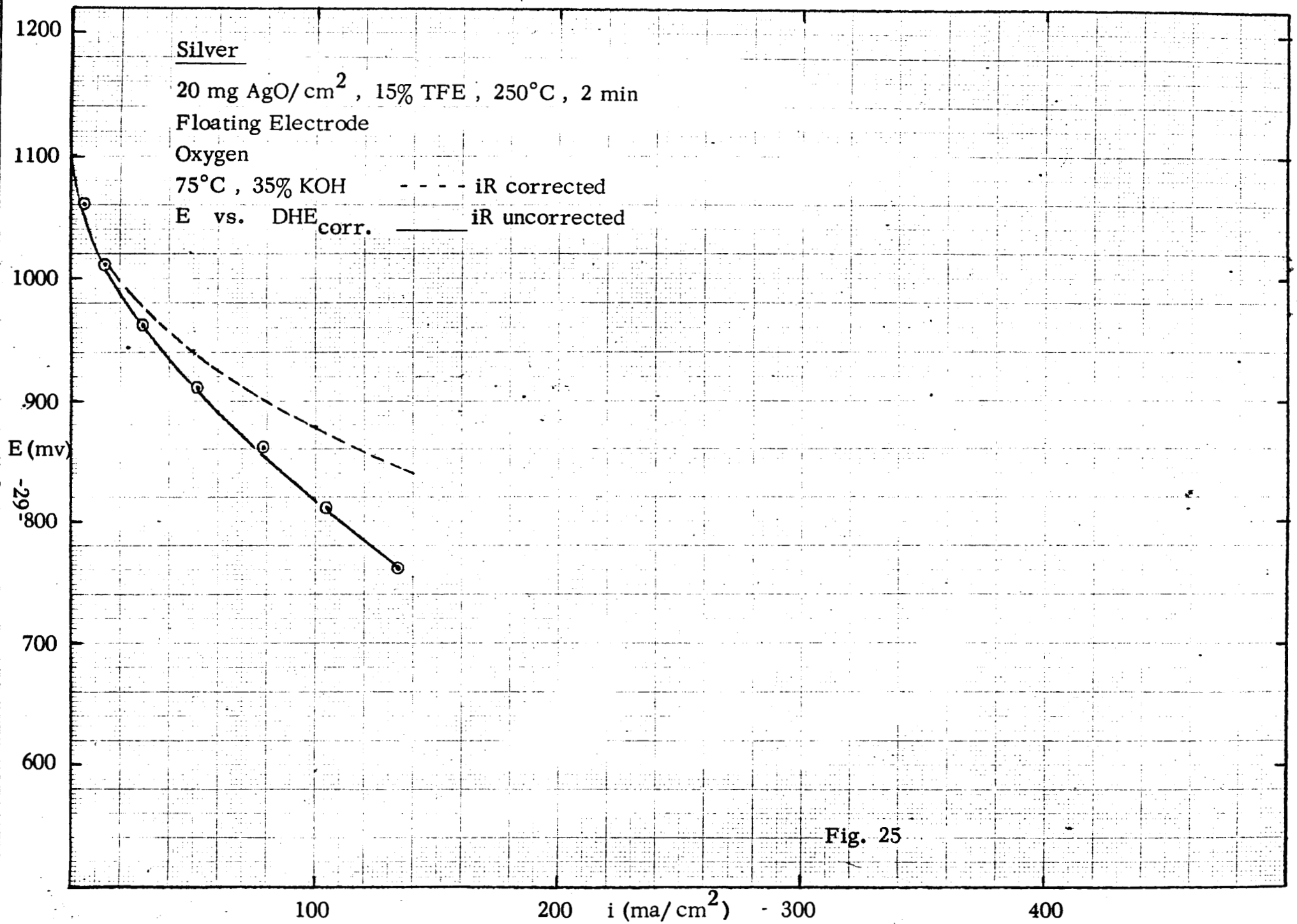

Fig. 25

K+E 10 X 10 TO THE CENTIMETER 46 1523
18 X 25 CM. MADE IN U.S.A.
KEUFFEL & ESSER CO.

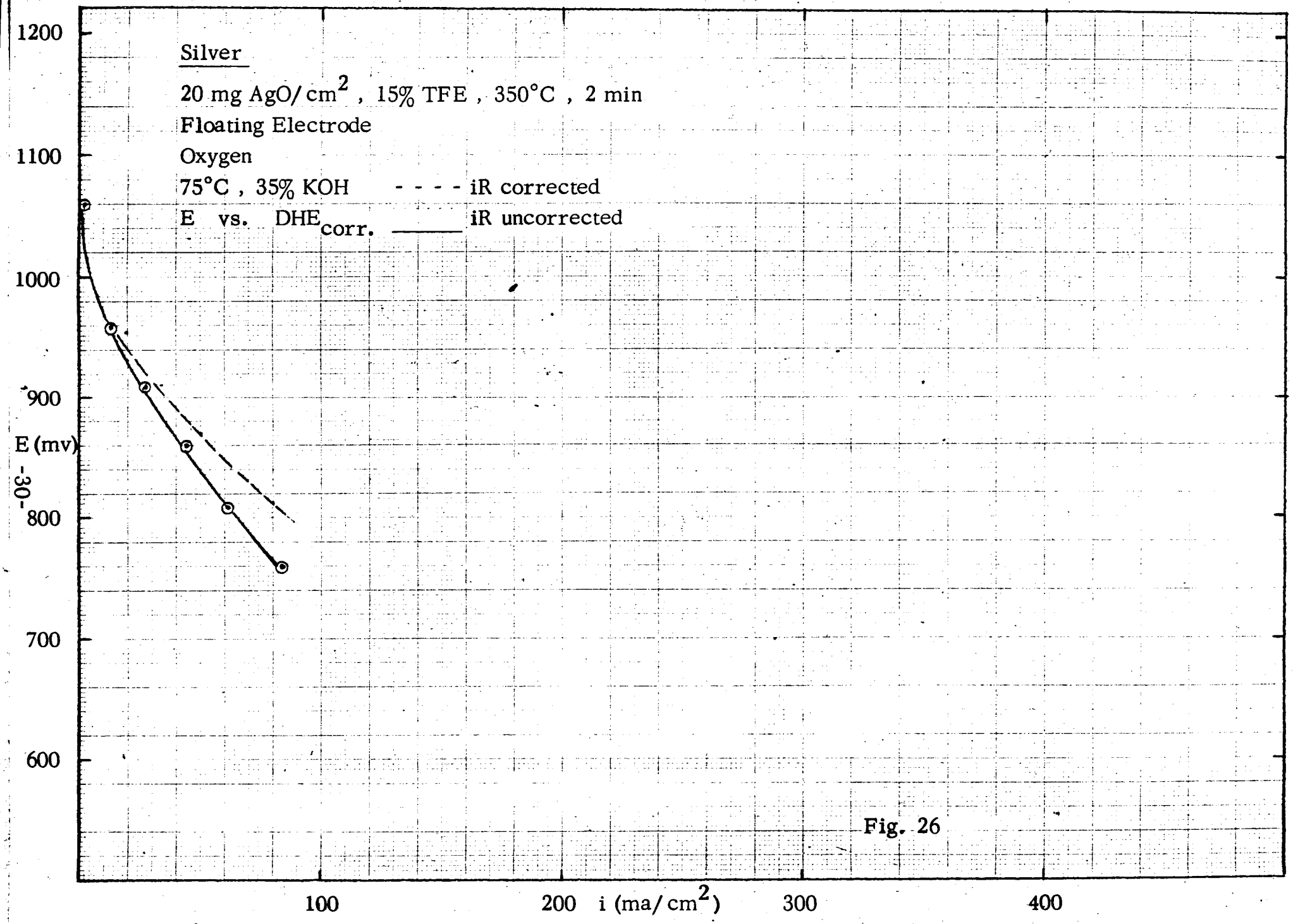

Fig. 26

18 X 25 CM. KEUFFEL & ESSER CO. MADE IN U.S.A.

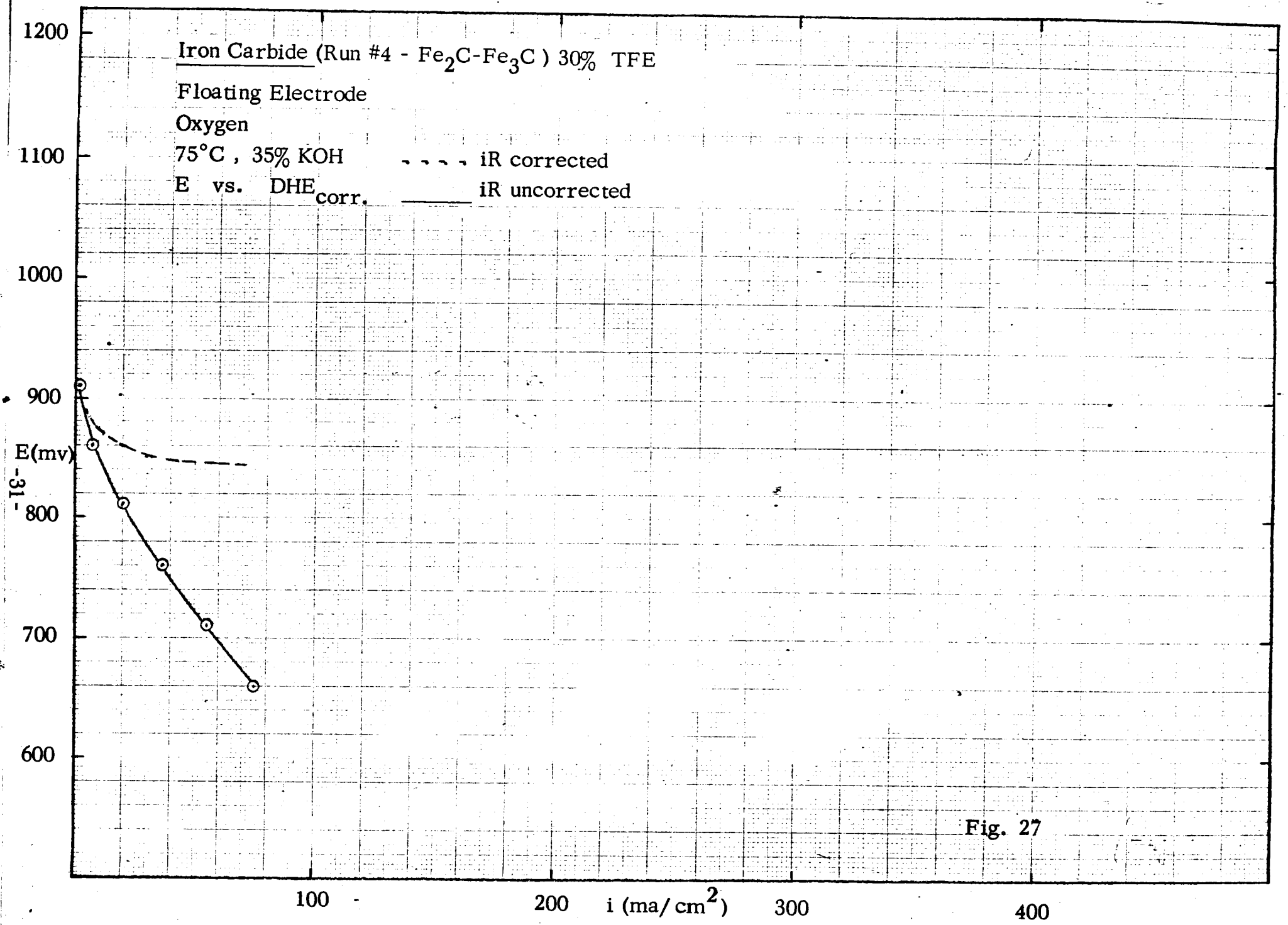

Fig. 27