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PART I. POTENTIAL TRANSIENTS

T. Huh and J.W. Evans

November 1985

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ELECTRICAL AND ELECTROCHEMICAL BEHAVIOUR OF FLUIDIZED BED ELECTRODES

Part I. Potential Transients

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ABSTRACT

A probe has been used to simultaneously measure the electrolyte and particle potentials within a fluidized bed electrode. The difference between the two signals then yielded the overpotential. Transients of all three potentials were stored by a microcomputer and the data processed to yield potential probability distributions and power spectra. Experiments were performed on beds of copper particles undergoing cathodic deposition from acidified sulfate solution and on beds of zinc coated particles undergoing deposition or dissolution of zinc with an alkaline zincate electrolyte. Both low frequency and wide band noise were observed in the potentials of copper particles while the former was much less for zinc coated polymer particles. An explanation was offered in terms of the hydrodynamics of the electrode, particularly the presence or absence of rising particle-free regions ("bubbles"). The distributions of time averaged potentials with position in the bed were measured and found to be in qualitative agreement with theory. Preliminary results on a moving bed electrode are reported.

INTRODUCTION AND PREVIOUS INVESTIGATIONS

There have been a large number of investigations of fluidized bed electrodes, particularly concerning the use of such for the electrodeposition of metals (a topic that has been recently reviewed (1)). Many investigators have concerned themselves with the mechanisms of charge transport in these electrodes. One of the first postulated mechanisms was a "collision mechanism" (2,3) where charge is transported by the particles making up the bed with collision resulting in sharing of charge between particles. Based on measurement of bed effective resistivities as a function of the frequency of an imposed alternating current, Sabacky and Evans (4) concluded that the collision mechanism was unlikely and suggested a "conductive" mechanism. In this mechanism, chains of particles were assumed to be in contact with one another and such chains would form a path for conduction. The chains would have a fleeting existence as they are broken and reformed by the motion of the particles in the bed. On those occasions when one (or more) member of a chain is in contact with a current feeder than the chain potential would approximate the current feeder potential and its members would be electrochemically active. Goodridge (5) and Plimley and Wright (6) have extended this concept by recognizing that chains that are isolated from the current feeder would show a bipolar behaviour. The latter investigators presented the results of a Monte Carlo simulation of the bed and compared their results to experimental measurements.

It appears that, no matter which of the two mechanisms is operative, the potential of a particle within the bed can be expected to show fluctuations about some time averaged value. Indeed, such fluctuations have been reported previously by Fleischmann and Kelsall (7), by Jiricny et al. (8) and by Plimley and Wright (5). Such fluctuations can be expected to affect the

kinetics of electrochemical reactions occurring in the bed and the morphology of any electrodeposit. For example, Jiricny and coworkers (9) have shown that overpotential fluctuations similar to those occurring at a particle in a fluidized bed electrode can affect the morphology of a zinc electrodeposit. The present paper describes the results of an experimental investigation of potential fluctuations in a fluidized bed electrode. Beds where copper is electrodeposited from acidic sulfate solution onto copper particles, and beds where zinc is deposited from alkaline solutions onto zinc coated polymer particles, have been studied. A companion paper (Part II) describes the results of experiments on electrical conduction within these beds.

EXPERIMENTAL APPARATUS AND PROCEDURE

Figure 1 depicts the probe used in this investigation for simultaneously measuring the potential of particles and electrolyte in a fluidized bed electrode. This dual probe is similar to that employed by Plimley and Wright (6) and consists of two insulated wires with exposed tips, both wires being enclosed in a glass tube through which electrolyte may flow at a slow rate. The tip of one wire is within the glass tube and therefore senses the electrolyte potential in the manner of a Luggin capillary. The tip of the other wire protrudes from the tube and is intended to sense the potential of the particles. The protruding tip has approximately the dimensions of the particles in the bed and it should therefore experience potential fluctuations similar to those of the particles in the bed, except for slow potential fluctuations resulting from the macroscopic movement of a particle across the bed. The difference in potential between the two tips is the local "instantaneous" overpotential. As depicted in Fig. 1 the probe is for use in a fluidized bed of zinc (or zinc coated) particles; copper wires were used for

measurements in beds of copper particles. The probe was mounted on a microscope stage supported on a calibrated stand; it could be positioned to within 0.1 mm in the horizontal direction and to within 1 mm in the vertical direction.

The cell and auxiliary equipment used in this investigation are sketched in Fig. 2. The probe signals were fed to a two channel digital oscilloscope (Nicolet 2090-III) connected to an Apple II microcomputer for data acquisition and processing. The fluidized bed electrode was of the rectangular side-by-side design (current flow predominantly in the horizontal direction) and was somewhat wider (45 mm from the diaphragm to the current feeder at the opposite side of the bed) than is normal for such electrodes, in order to permit measurements over a wide range of position. The other dimensions of the bed (when fluidized) were 70 mm by 180 mm high.

Copper was deposited from copper sulfate solution, containing 25 kg/m^3 of copper, that had been prepared by dissolving the salt (Reagent Grade, Mallinckrodt Inc.) in distilled water and acidifying with sulfuric acid (ditto) to 50 kg/m^3. The anolyte was produced from distilled water and sulfuric acid (50 kg/m^3) and, by use of separate anolyte and catholyte reservoirs and a diaphragm (Daramic, W. R. Grace Corp.) of low permeability, was kept separate from the catholyte. Copper particles (Alcan Metal Powders) were of 0.5 mm nominal diameter. Copper particles were pre-treated by cleaning in dilute nitric acid, rinsing in water and drying in an oven. Immediately before use they were rinsed in dilute sulfuric acid to remove any oxide coating. A graphite current feeder and a DSA anode (Eltech Corp.) were connected to an HP DC power supply operated in the constant current mode.

For experiments on zinc, polymer particles (0.3-0.4 mm diameter) with a 1 μm nickel coating followed by 1 μm of cadmium, followed by up to 125 μm of

zinc, were used. These particles were obtained from Sorapec Corp. and are intended for energy storage purposes. A few experiments were carried out using copper particles which were coated with zinc in a prior deposition experiment. Sorapec particles were rinsed several times in distilled water and then in dilute potassium hydroxide solution immediately before use. A graphite current feeder and a platinized titanium mesh counter electrode were used in this part of the investigation where both electrodissolution and electrodeposition of zinc were studied. Both electrolytes were prepared from 5M potassium hydroxide solution (Reagent Grade, Mallinckrodt Inc.). Zinc was first anodically dissolved in the solution and then current was reversed to deposit it. Samples were taken periodically to determine the zincate concentration by titration with EDTA.

The experimental procedure consisted of filling each reservoir with electrolyte, turning on the pumps, adjusting the probe position and adding particles to the fluidized bed side of the cell. The catholyte flowrate was adjusted to bring the bed to the desired expansion, the current turned on and adjusted to the desired level, and (after a few moments to allow for a quasi-steady state to be reached) data acquisition was commenced. During the experiments the cell potential was recorded continuously by a chart recorder. There was no change in cell potential observable on the recorder, reflecting the fact that the electrolyte reservoirs had sufficient volume that only small concentration changes occurred in the electrolytes during the course of a run.

Preliminary experiments showed that a 10 ms sampling interval provided satisfactory results; both slow (with a period of the order of 1 second) and more rapid fluctuations were observed. 10 ms was a compromise between the desire to measure the fluctuations over as broad a frequency range as possible and the need to represent the slow fluctuations with a manageable number of

data points. With repeated acquisition of sets of data (each consisting of 1024 points) at a 10 ms sampling interval, the variation in the mean of the electrolyte and particle potentials was ±4 mV while the mean overpotential showed variations of ±0.2 mV. Variations in the standard deviations were ±2 mV and ±1 mV respectively.

Following storage of particle and electrolyte potentials in the microcomputer this device took differences to obtain overpotential data. All three sets of potential data were then processed to obtain potential probability distributions and power spectra. The latter were calculated by the fast Fourier transform method. The results were then plotted or printed.

Further details concerning the apparatus and procedure can be found in the dissertation (10) on which this paper is based.

RESULTS AND DISCUSSION

Copper particles

Fig. 3 showed representative data obtained for copper deposition experiments. The data was collected from the center of the bed. Note the slow potential fluctuations of both the particles and the electrolyte, fluctuations which are absent from the local overpotential. The slow fluctuations will henceforth be referred to as "flicker noise". It should also be noted that the vertical scale of the overpotential plot is different from that of the others and therefore the overpotential is showing much less fluctuation. Finally, the overpotential is seen to be both anodic and cathodic in agreement with the concept that there exist bipolar chains of particles in the bed. Consider a cluster of particles isolated from the current feeder. The relative values of conductivity of the electrolyte and particles will develop an equipotential within the particulate phase while the

electrolyte displays a potential gradient. These different distributions develop an anodic region on one side of a particle and a cathodic region on the other. When the probe contacts the anodic region it senses an anodic overpotential even when the overall reaction in the bed is cathodic.

Figs. 4, 5 and 6 illustrate the results of processing the data of Fig. 3. The different scales used in these figures should be noted. Vertical marks on the horizontal axes of the upper plots indicate mean values. The particles and electrolyte are seen to be at a positive potential with respect to the current feeder with excursions to more than a hundred millivolts from the mean being common. In contrast the local overpotential rarely shows excursions of more than 20 mV from its slightly cathodic mean. The power spectra for the particles and electrolyte display the flicker noise already mentioned while this noise is absent from the power spectrum of the overpotential where there is wide band "white" noise. The white noise is also present in the power spectra of the particle and electrolyte potential.

A possible explanation for the flicker noise is the occurrence of "bubbles" in a bed of copper particles fluidized by an electrolyte. What is referred to is <u>not</u> gas bubbles but rather regions of the bed that are free of particles. These regions rise through the bed and "burst" at the surface of the bed much as a gas bubble might; their existence is well recognized in the literature on fluidized beds and such beds are characterized as "smooth", "transition" or "bubbling" depending on the extent of occurrence of these voids. Davidson and Harrison (11) have presented a bed behaviour diagram enabling the prediction of the presence or absence of bubbles as a function of particle size and densities. This diagram predicts bubbling for the copper particles used in the present study and such bubbles could be visually observed at the bed surface. The same diagram predicts a maximum stable

bubble size of approximately 15 mm. This is the maximum size the bubbles should reach as they grow by coalescence after leaving the distributor at the bottom of the bed.

Fig. 7 shows the probability distribution and power spectrum of the particle potential at the center of the bed but with a lower catholyte flow rate and therefore lower bed expansion (13%) than that of Fig. 4 (25%). The mean particle potential is now closer to that of the current feeder reflecting the fact that a less expanded bed is more conductive (4). Furthermore, the excursions of the particle potential about the mean and the noise are much less, indicating their hydrodynamic origin. Table I summarizes the results for these two bed expansions and an intermediate one. Also appearing in this table are the mean and standard deviation of the overpotential. It is seen that these are little affected by bed expansion while both the mean and standard deviation of the particle potential increase greatly with bed expansion.

The results of measurements 60 mm below the center of the bed appear in Fig. 8 for the particles. The bed expansion is 25% and these results should be contrasted with those of Fig. 4. This region of the bed is just above the distributor and it is seen that the potential fluctuations at this position are very different from those in the center of the bed; the mean particle potential is lower at the bottom of the bed while the flicker noise is almost absent. An explanation of the former effect is that this position is 10 mm below the active "window" area of the diaphragm and is therefore in a region of low current density. The variation of mean particle potential with vertical position is depicted in Fig. 9 where it is seen that the potential reaches a maximum somewhat above the center of the active window area. The near absence of flicker noise at the bottom of the bed might be explained by

the hypothesis that low frequency potential transients are due to bubbles. Such bubbles grow by coalescence as they move up from the distributor and it is likely that at the bottom of the bed they are of insufficient size to affect the potentials. The coefficient of variation of the particle potential (ratio of its standard deviation to time averaged value) was 0.19 $\pm$ 0.04 throughout the height of the bed, except for the lowest positions (40 and 60 mm below the bed center) where the coefficient was less than half this value.

Fig. 9 also shows the variation of the time averaged overpotential with vertical position. The low absolute values outside the window area are indicative of the low current densities in these regions; consequently the particles in these regions are in near equilibrium with the electrolyte. The authors are uncertain as to the cause of overpotential variation with position within the region of the bed opposite the active window area.

Sorapec particles

In this phase of the investigation the particle and electrolyte potentials were measured with respect to the electrolyte potential of the cell diaphragm, this being measured by a Luggin capillary on the fluidized bed side of the diaphragm. Fig. 10 depicts the transients of the particle, electrolyte and overpotential in a bed of Sorapec particles, wherein zinc is being deposited from an electrolyte containing 15 g/l of zinc. This figure should be contrasted with Fig. 3 (obtained for a bed of copper particles with the same superficial current density and a somewhat lower bed expansion). Noting the differences in the vertical scales it is immediately apparent that the bed of Sorapec particles suffers much smaller potential excursions than that of copper particles. This is reflected in the probability distribution and power spectrum for the particles (Fig. 11, to be contrasted with Fig. 4). It should be noted however that, although low, the noise in the overpotential shows a

slight flicker component; comparing the power spectrum of the overpotential (Fig. 12) with that for the copper particles (Fig. 6) the former shows a rise towards lower frequencies whereas the latter is almost uniformly distributed over the 50 Hz frequency range examined.

In explaining the difference in behaviour between the $Cu/CuSO_4/H_2SO_4$ bed and the $Zn/K_2Zn(OH)_4/KOH$ bed two important factors should be recognized. The two types of particle have different densities (8 g/cm^3 for copper versus approximately 3 g/cm^3 for the Sorapec particle) which results in different fluidization velocities and different hydrodynamic characteristics (presence or absence of bubbles). Secondly, the electrochemical reactions are different and may be expected to display different kinetics.

The Sorapec bed was observed to be relatively free of bubbles and uniformly fluidized from top to bottom. This is consistent with the bed behaviour diagram of Davidson and Harrison (11) which predicts that beds of Sorapec particles should be in a transition regime between smooth and bubbling fluidization. That diagram predicts a maximum stable bubble size of approximately 4mm. This low level of bubbling is consistent with the low level of flicker nosie in the particle and electrolyte potential of the Sorapec bed.

The overpotential data for the Sorapec bed have two characteristics requiring explanation: the relatively narrow distribution about the time averaged value (contrasting the upper halves of Figs. 12 and 6) and some tendency for the noise in the overpotential to be low frequency, rather than white noise (contrasting the lower halves of these two figures). The former may be explained in terms of the exchange current densities. The instantaneous overpotential at a particle in the bed is the consequence of two phenomena: the departure from equilibrium (zero overpotential) due to fleeting

indirect electrical contact with the current feeder (or membership in a bipolar chain) and the electrochemical reaction at the particle surface which tends to restore the equilibrium. The (average) magnitude of the fluctuations will therefore be less if the electrochemical reaction is faster. Zinc deposition from zincate solutions has a higher exchange current density, reportedly in the range 8 - 370 mA/cm^2 (12), than copper from acid sulphate solutions where the exchange current density is approximately 3 mA/cm^2 (13). In other words, for the same overpotential there is a much greater tendency to reduce the overpotential (fluctuation) for Sorapec particles, than for copper particles.

Only a tentative hypothesis can be offered for the presence of flicker noise in the overpotential for Sorapec particles. The wide band noise observed for both copper and Sorapec beds is presumed to be due to the stochastic nature of particle-particle collisions and the effect of such particles on chain formation. It seems likely that such noise would be distributed throughout a broad frequency range, the nature and breadth of this distribution being dependent on those particle characteristics (density, elasticity, size, roughness) and electrolyte characteristics (density, viscosity, velocity, turbulence) that are involved in the dynamics of particle motion and collision. The apparent uniformity of the white noise for copper particles up to 50 Hz need not imply uniformity beyond 50 Hz. The hypothesis then is that the tendency of the overpotential of Sorapec bed towards low frequency noise is merely a consequence of the relatively slow collision process for Sorapec particles.

Measurement of transients in a bed of Sorapec particles operated anodically yielded results (10) that were very close to those obtained with the same bed operated cathodically at the same bed expansion and superficial

current density (with obvious reversal of sign of the mean values). This is consistent with the observation of Bockris et al. (14) that the mechanism of anodic and cathodic reaction of zinc in alkaline solution is the same.

Increased bed expansions resulted in broader probability distributions of the particle potential and a more negative time averaged value for zinc deposition onto Sorapec particles. The latter is consistent with a higher effective bed resistivity at higher bed expansions. Increased bed expansions had little effect on the overpotential. Neither the time averaged particle potential, nor its standard deviation showed much variation with vertical position within the region of the bed opposite the active window area, the same held true for the overpotential.

Figs. 13 and 14 contrast the particle potential transients for zinc coated copper particles and Sorapec particles. The zinc coated copper particles would show bubbling fluidization and this is revealed in the much higher noise level for these particles. The particle potential transients appear similar to those of copper particles in the $Cu/CuSO_4/H_2SO_4$ system whereas the overpotential transients were similar to those of the Sorapec particles.

The variation of the time averaged particle potential with distance from the current feeder is depicted in Fig. 15 for Sorapec particles undergoing zinc deposition. The nearly linear plot is indicative of the deposition reaction being confined to the two sides of the bed (assuming the bed to have uniform effective resistivity). This is in agreement with Fig. 16 where the variation of the time averaged overpotential with position is displayed. Theoretical models for porous electrodes e.g. that of Newman and Tobias (15) and for fluidized bed electrodes e.g. that of Sabacky and Evans (16) have predicted the corresponding U shaped distribution of local reaction rate.

Experimental confirmation of this variation of deposition rate (in copper electrodeposition experiments) with an inactive zone in the middle of the bed has been provided by Masterson and Evans (17). Fig. 17 reveals that there is a small variation of the standard deviation of the particle and electrolyte potential across the bed and a smaller variation of the standard deviation of the overpotential.

Preliminary experiments were carried out on a moving bed electrode. This electrode contained downward moving particles with upflow of electrolyte being insufficient to fluidize the particles. Particles fell through a slot at the bottom of the bed and were recycled to the top in a separate conveying section. Details of this apparatus are contained in Huh's dissertation (10). Fig. 18 shows potentials measured in this electrode during copper deposition onto copper particles from acidified sulfate solution and note should be made of the vertical scale. Clearly transients are virtually absent in this electrode. Furthermore the particles are essentially at uniform potential; what variation of particle potential is discernible in Fig. 19(a) is consistent with reaction taking place largely in the part of the bed remote from the current feeder. Accordingly the local overpotentials are most negative in this region; see Fig. 19(b). This is as expected, the moving bed electrode has a very low effective resistivity. Consequently the "path of least resistance" from the anode to the current feeder is through the particles, rather than the catholyte, resulting in much of the reaction taking place in the region of the bed closest to the anode (opposite the current feeder).

CONCLUDING REMARKS

The present investigation has been concerned with the variations of particle and electrolyte potentials and their difference (the overpotential)

in fluidized beds of copper and zinc coated particles. Variation with time, with position and with bed parameters (e.g. bed expansion) have been measured. The results strongly suggest that the observed particle potential transients are partly due to the presence of bubbles in the fluidized bed. These bubbles (which are voids rising in the bed rather than gas bubbles) give rise to low frequency noise in the particle potential of the copper particles and zinc coated copper particles. This flicker noise is much less for zinc coated polymer particles. This hypothesis is supported by the visual observation of much fewer bubbles in beds of the last named particles, by predictions of the presence of bubbles due to a correlation of Davidson and Harrison, by the absence of the transients in a moving bed electrode, and by measurements of effective bed resistivity described in Part II.

The overpotential transients show some flicker noise for zinc coated polymer particles and less for copper particles. It is hypothesized that the wide band noise of these transients is due to the stochastic particle-particle collisions. The overpotentials are frequently anodic, even in a bed which is nominally cathodic. This is consistent with a conductive (bipolar) mechanism for charge transport in fluidized bed electrodes. The effects of such fluctuating potentials on the morphology of a zinc electrodeposit have been investigated in our laboratory using a rotating disc electrode and are the subject of a separate publication (18). Variation of the time averaged overpotential with position in the bed is consistent with theoretical expectations.

ACKNOWLEDGMENT

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Table I
Effect of bed expansion on potential transients - copper particles - 200 mA/cm^2

Bed expansion %	Time averaged particle potential (mV)	Standard deviation (mV)	Time averaged overpotential (mV)	Standard deviation (mV)
13	138	11	-1.5	10
17	160	31	-1.4	13
25	234	53	-1.7	14

FIGURE CAPTIONS

1 Sketch of dual probe for simultaneously measuring local particle and electrolyte potential in fluidized bed.

2 Sketch of cell with fluidized bed electrode employed in this investigation, together with associated electrolyte and electrical systems.

3 Particle, electrolyte and overpotential transients as measured in the center of a fluidized bed of copper particles undergoing electrodeposition of copper at a superficial current density of 200 mA/cm^2. Bed expansion 25%. Potential measured with respect to copper current feeder.

4 Analysis of the particle potential data of Fig. 3.

5 Analysis of the electrolyte potential data of Fig. 3.

6 Analysis of the overpotential data of Fig. 3.

7 Analysis of particle potential data obtained in experiment similar to that of Fig. 3 but at bed expansion of 13%.

8 Analysis of particle potential data obtained in experiment similar to that of Fig. 3 except measurements made 6 cm below the bed center.

9 Vertical variation of time averaged local overpotential (η) and particle potential (Φ_p) for conditions similar to those of Fig. 3.

10 Particle, electrolyte and overpotential transients measured in center of a fluidized bed of Sorapec particles undergoing zinc deposition from alkaline electrolyte at a superficial current density of 200 mA/cm^2. Bed expansion 30%. Potential measured with respect to electrolyte at diaphragm.

11 Analysis of particle potential data of Fig. 10.

12 Analysis of overpotential data of Fig. 10.

13 Analysis of particle potential data for experiment similar to that of Fig. 10 but using Zn coated Cu particles at 100 mA/cm^2.

14 Analysis of particle potential data for experiment similar to that of Fig. 13 but using Sorapec particles.

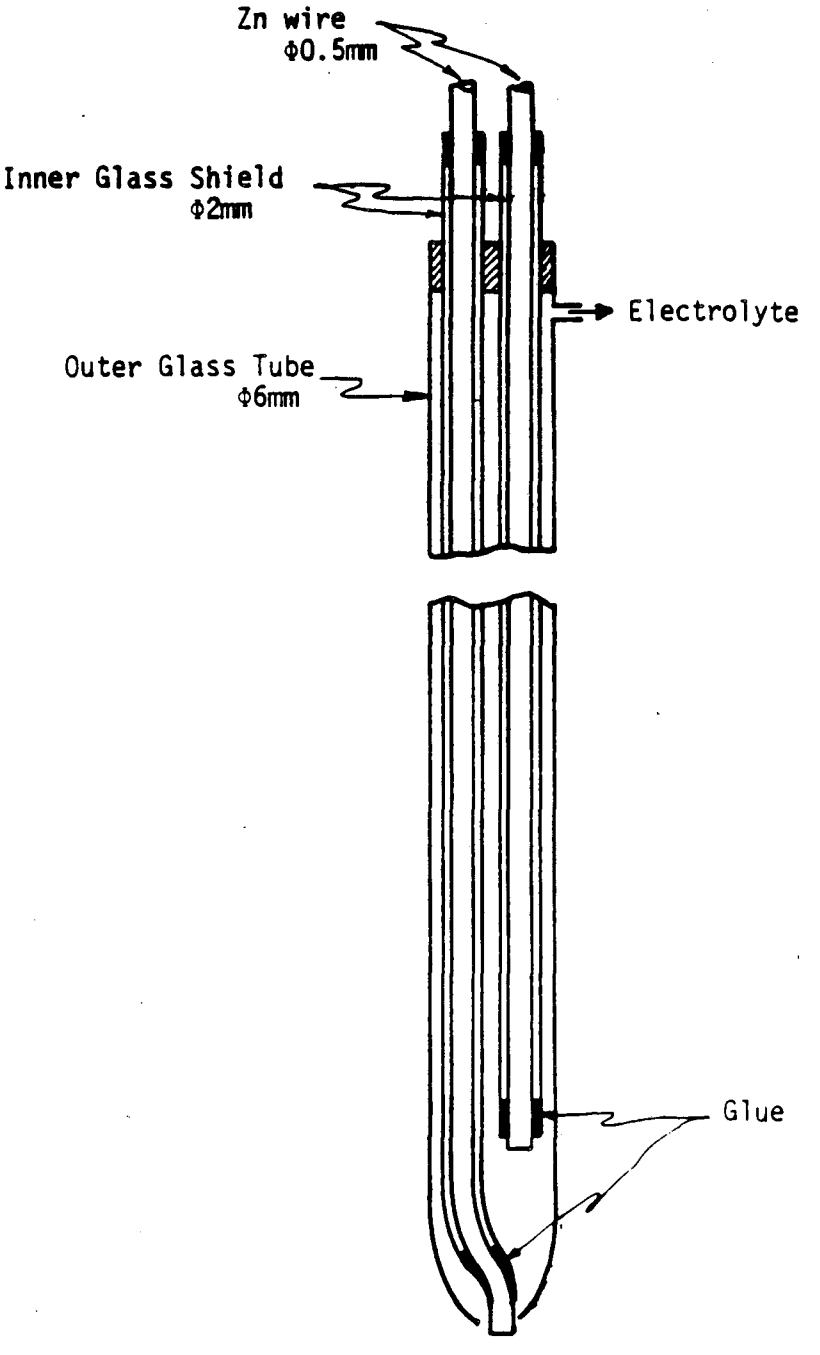
15 Variation of time averaged Sorapec particle potential with horizontal position in bed. 25% bed expansion. 100 mA/cm^2.

16 Variation of time averaged overpotential with horizontal position in bed.

17 Variation of standard deviations of potentials with horizontal position in bed.

18 Particle, electrolyte and overpotential transients measured in the center of a moving bed of copper particles undergoing copper electrodeposition. Superficial current density of 200 mA/cm^2.

19 Variation of (a) particle potential and (b) local overpotential with horizontal position in moving bed of Fig. 18 at two superficial current densities.



XBL 847-3264

Fig. 1

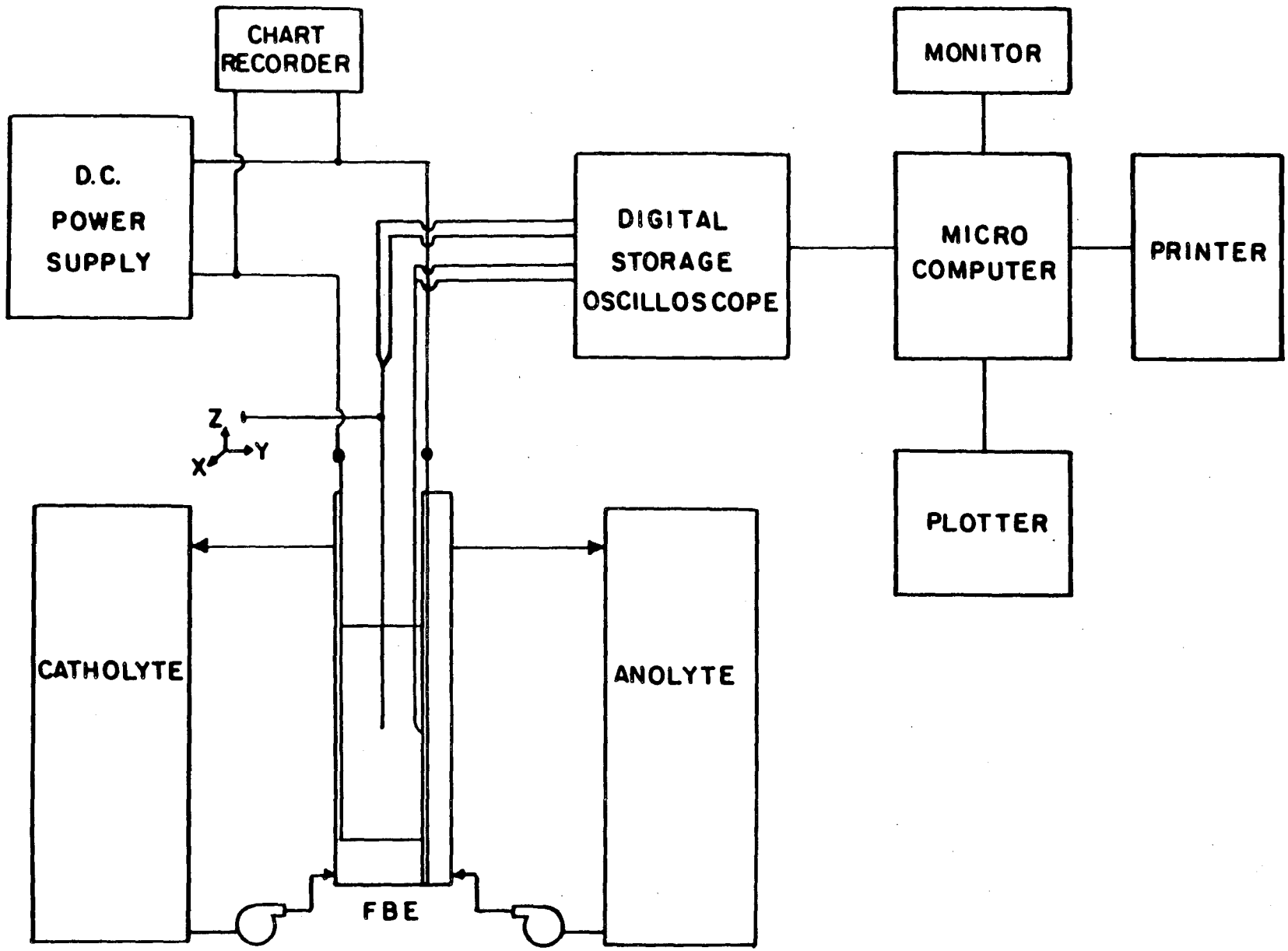


Fig. 2

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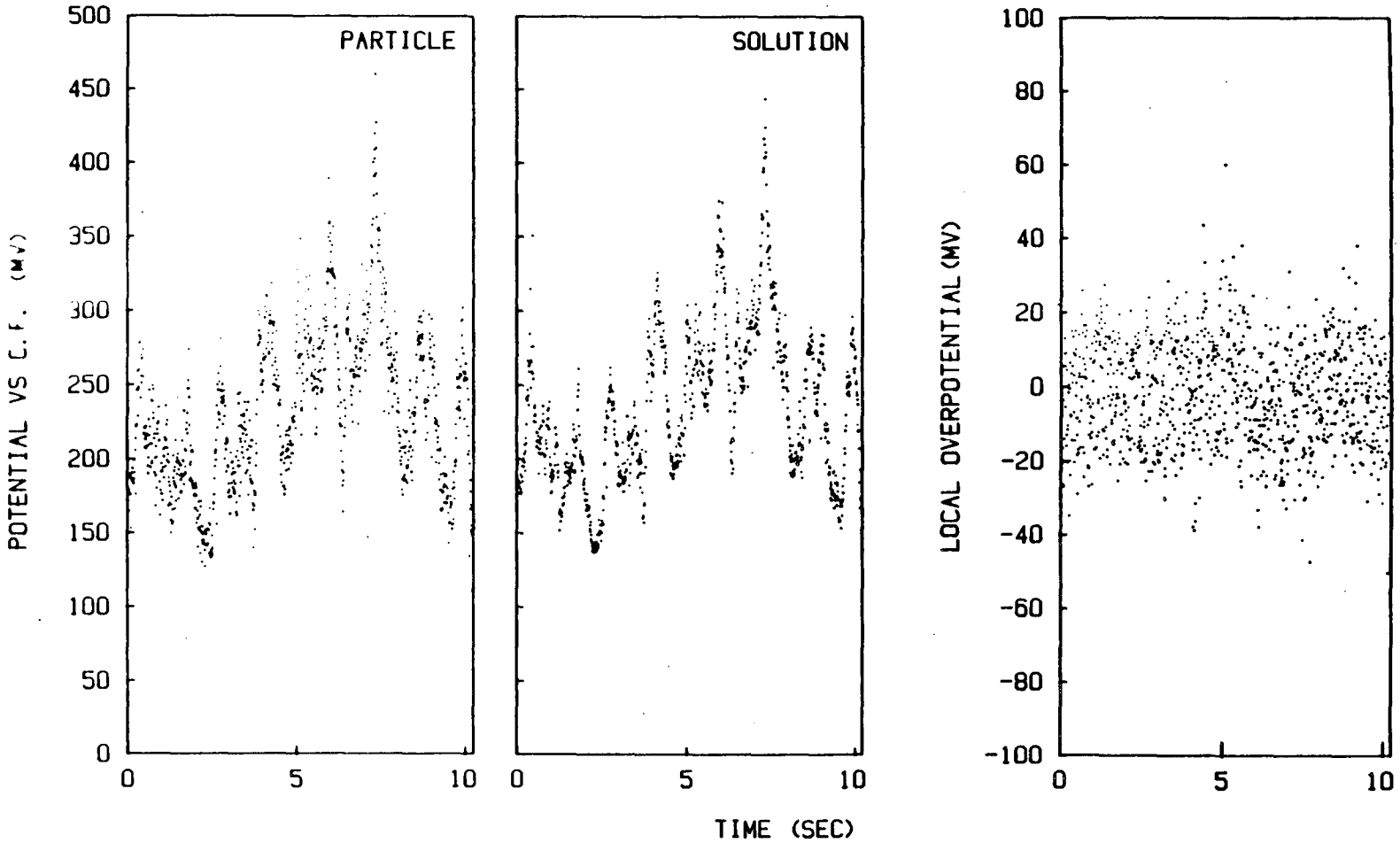

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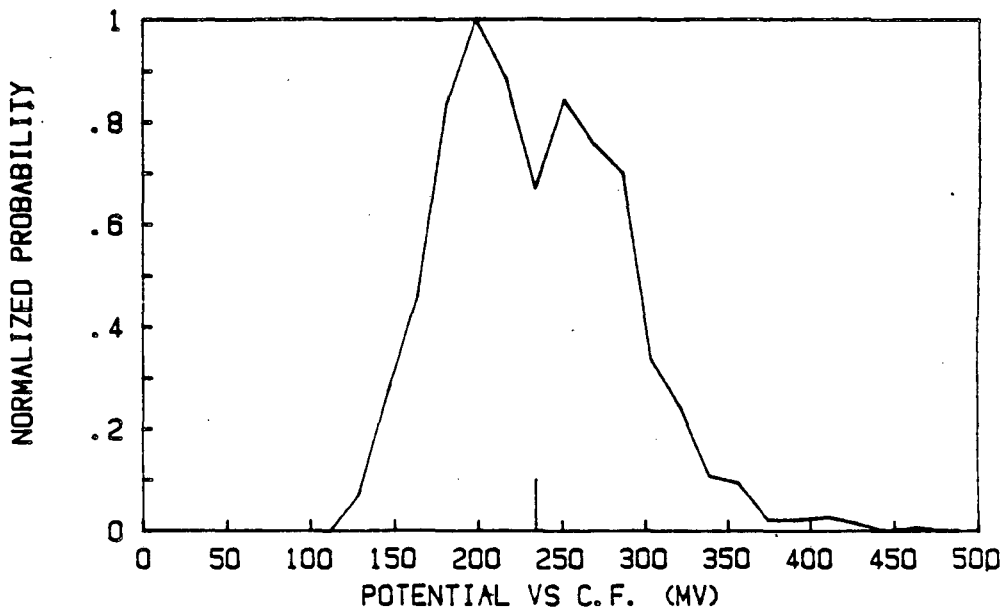
Fig. 3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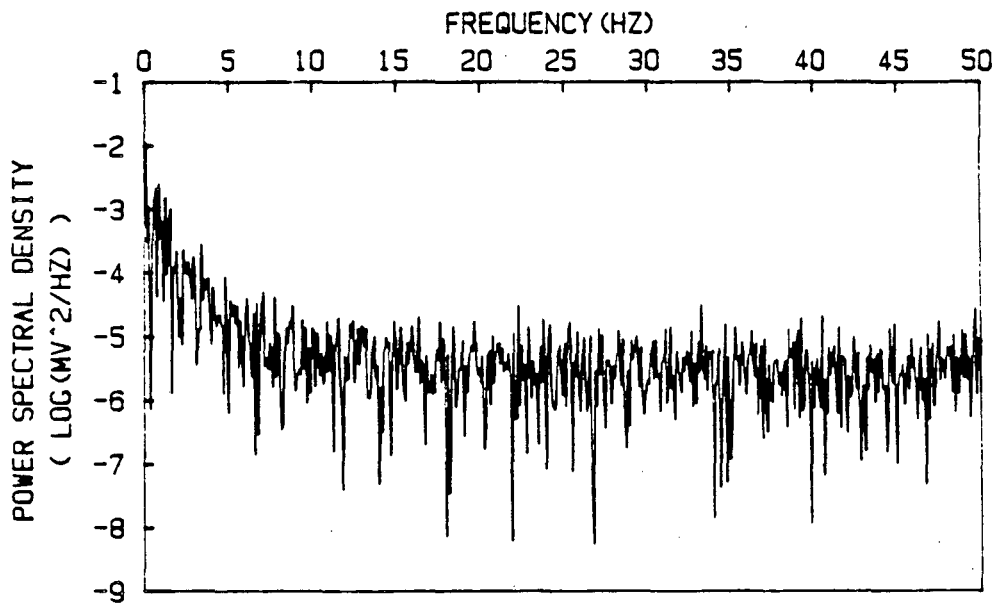
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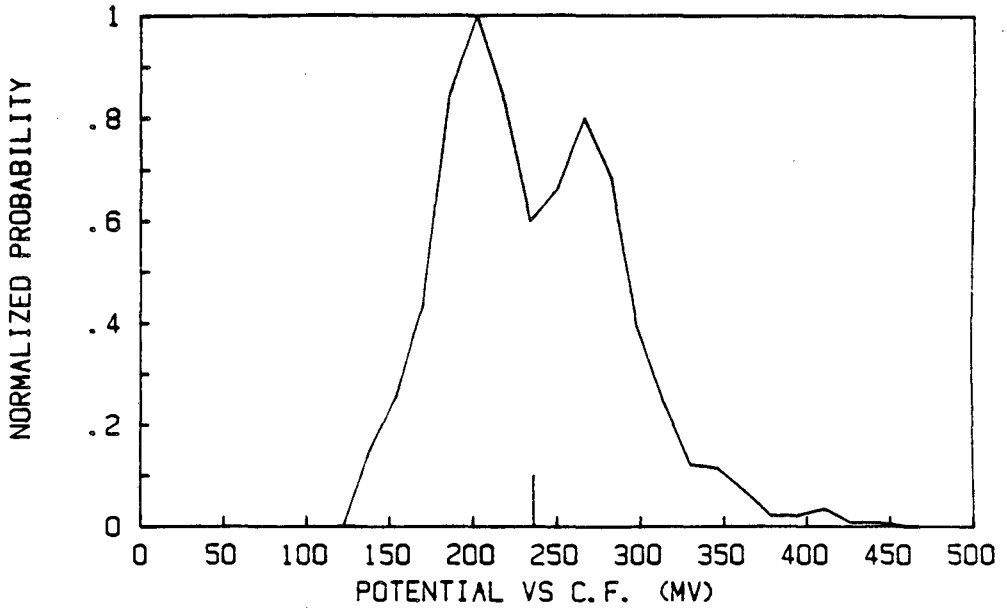
Fig. 4



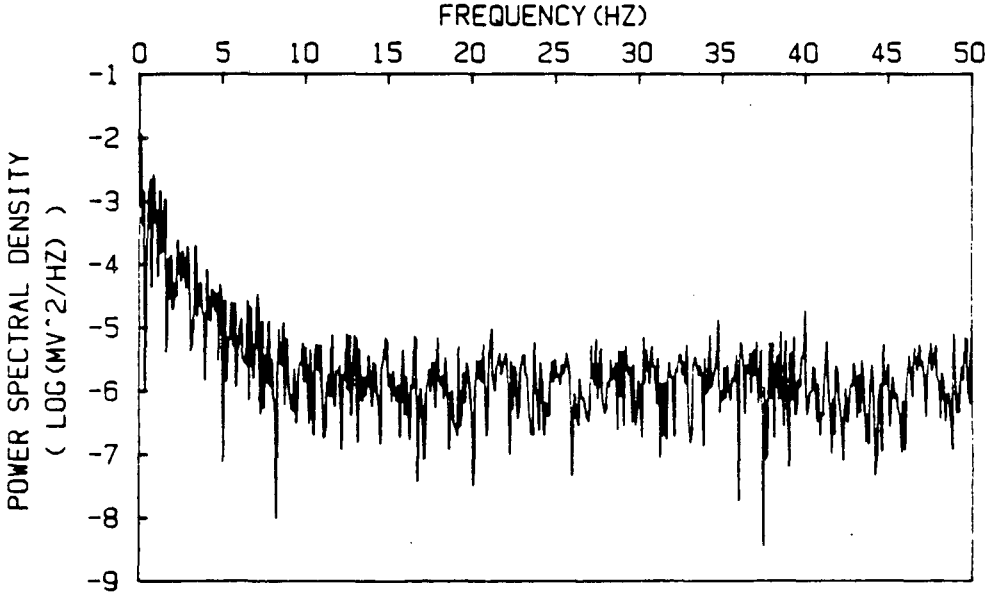


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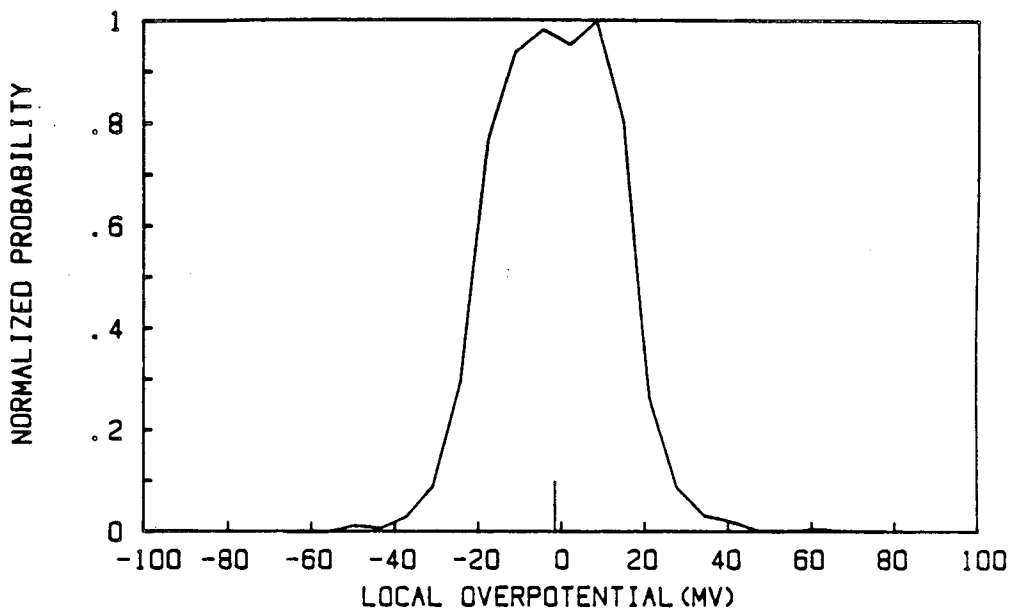
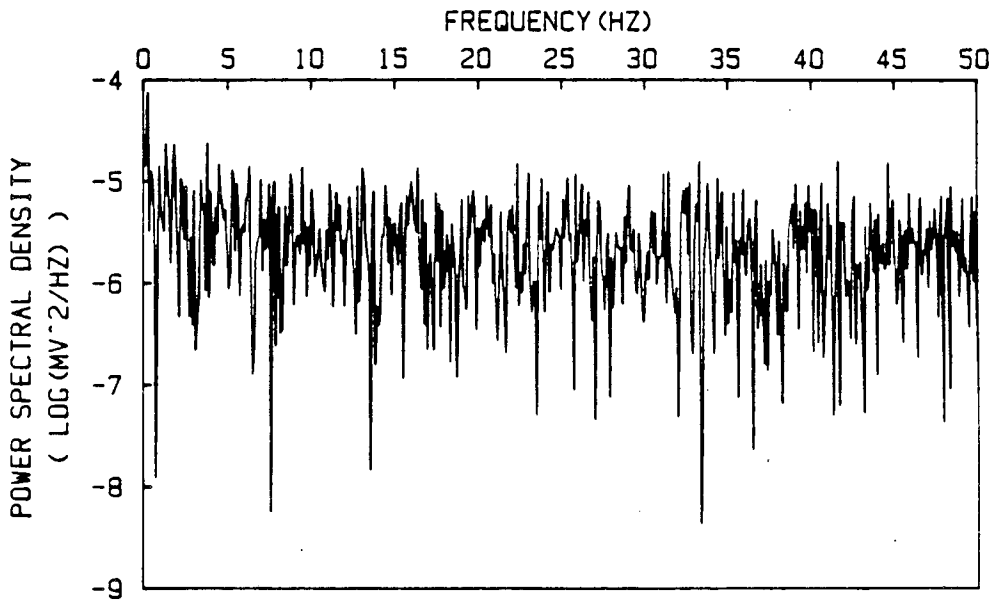
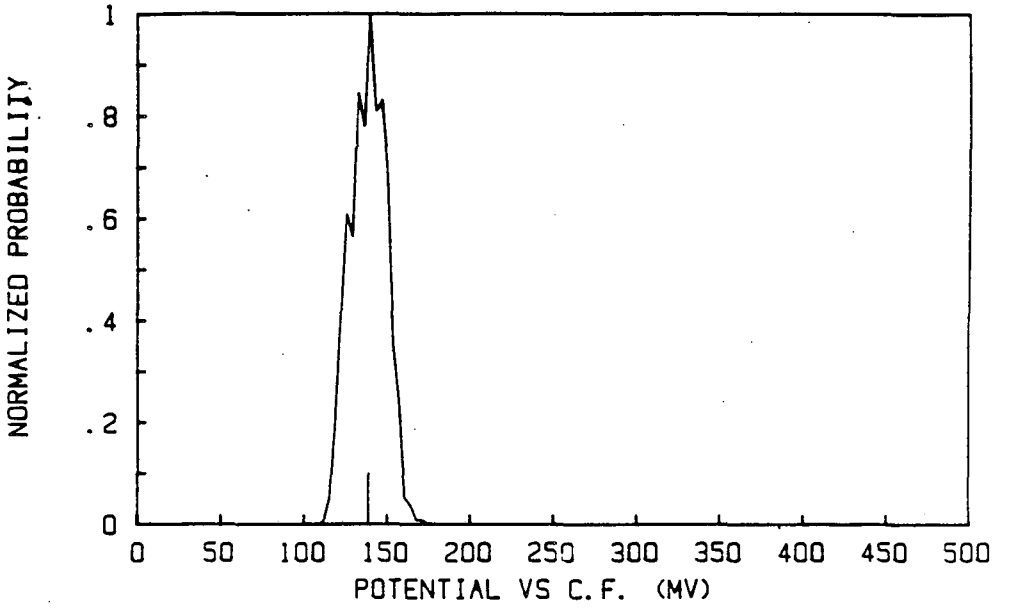
Fig. 5

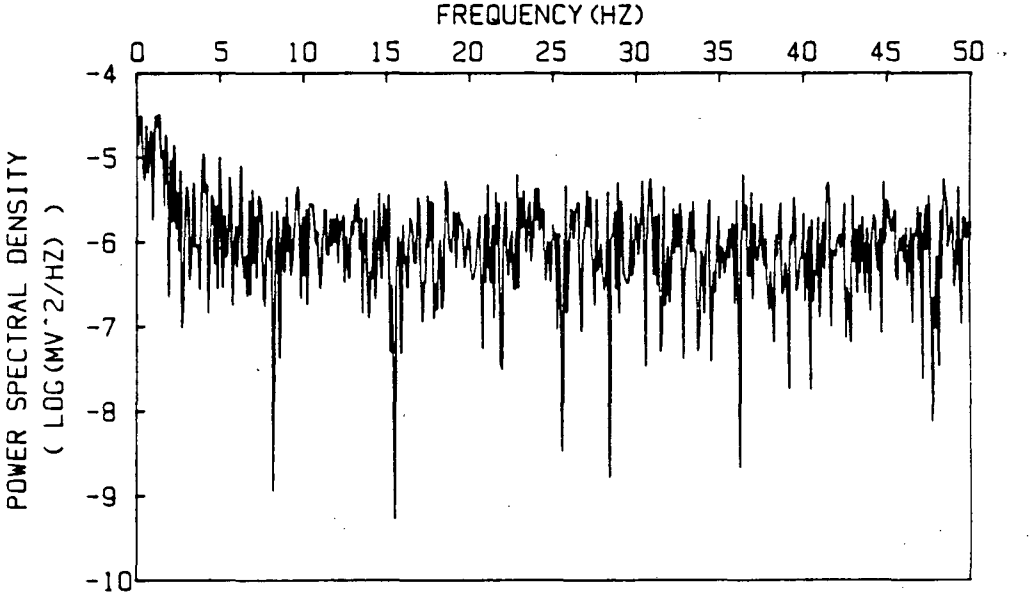




XBL 8510-4170

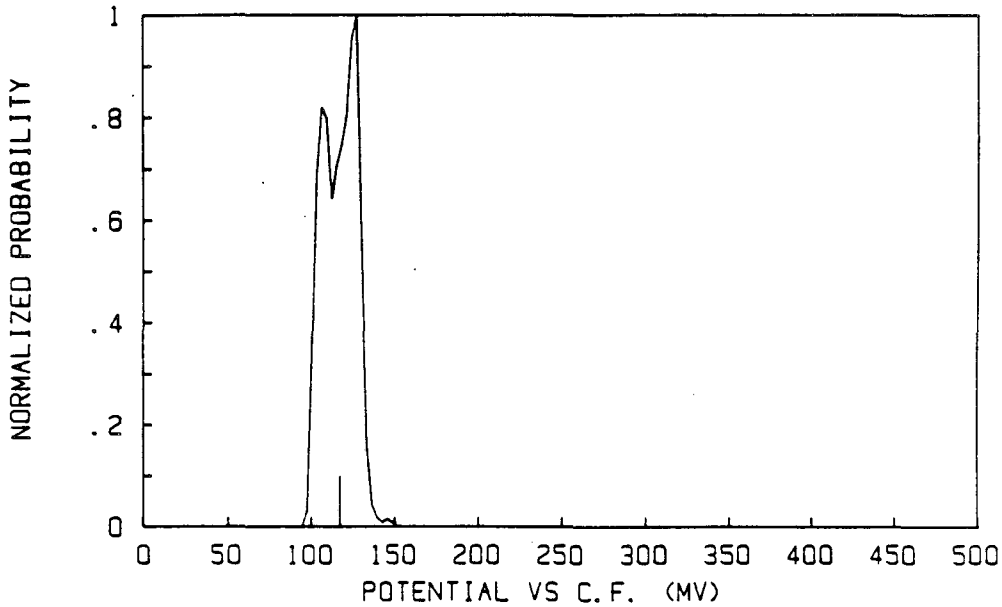
Fig. 6

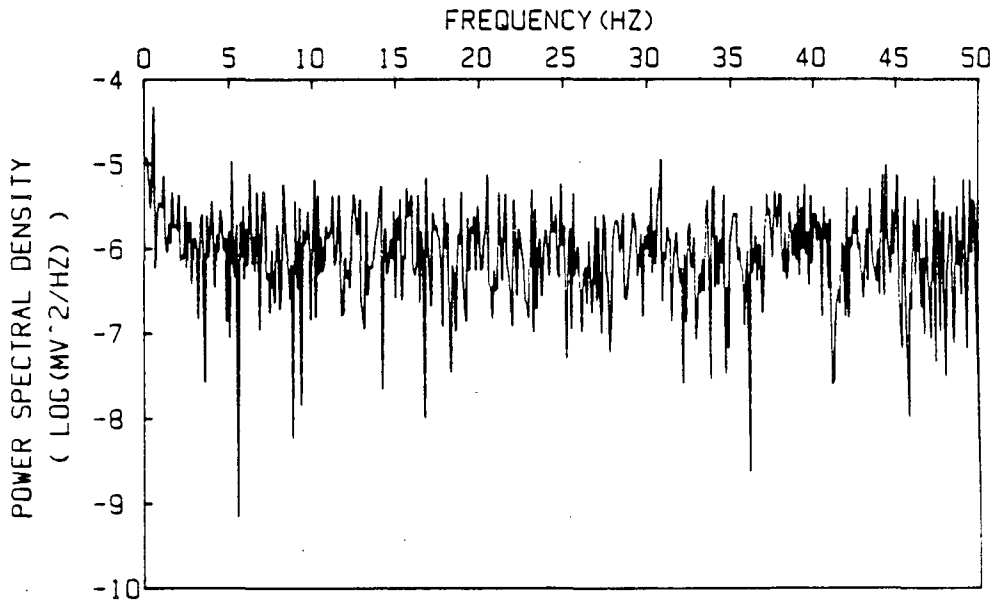




XBL 8510-4171

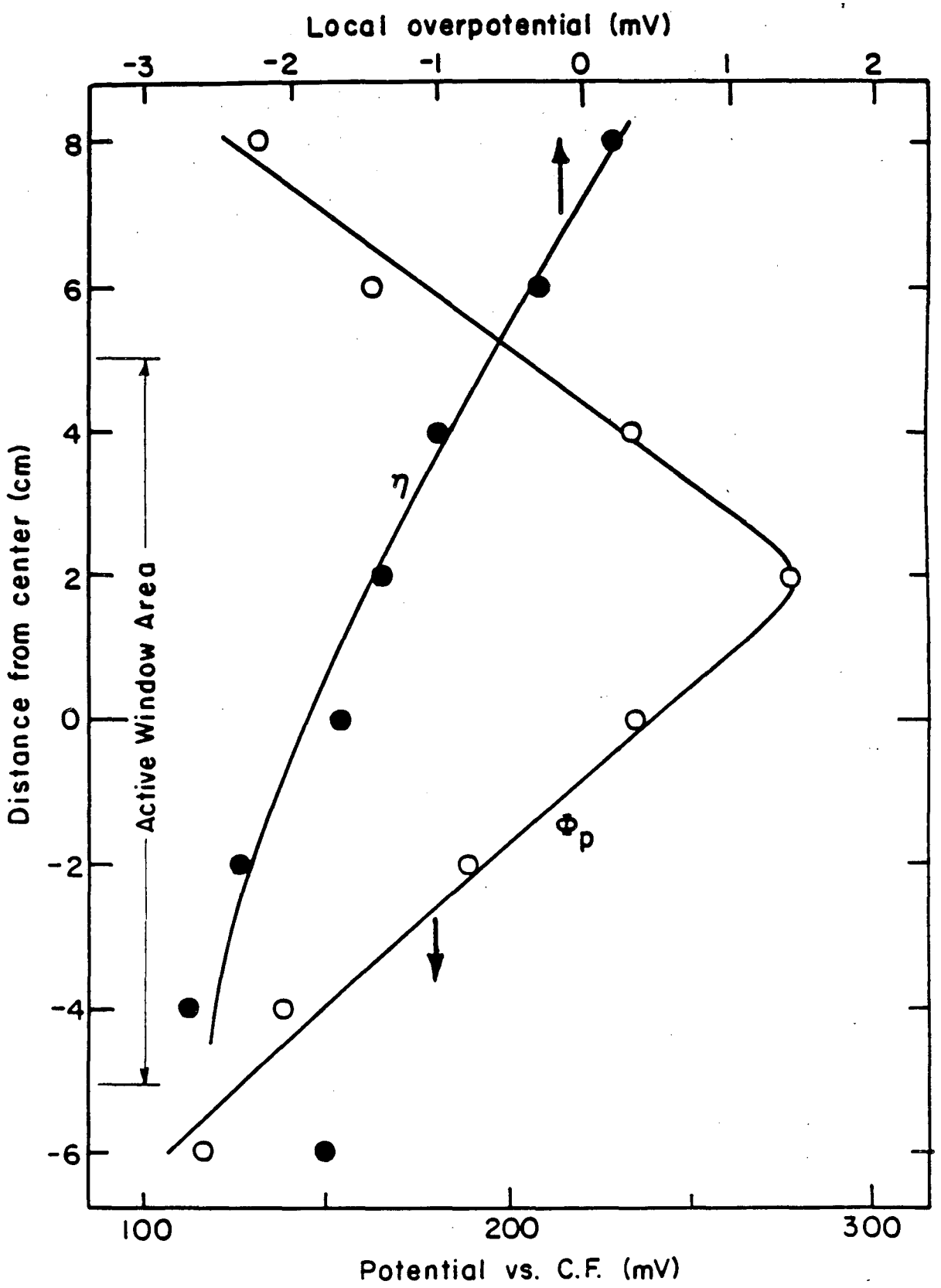
Fig. 7





XBL 8510-4172

Fig. 8



XBL 8510-4173

Fig. 9

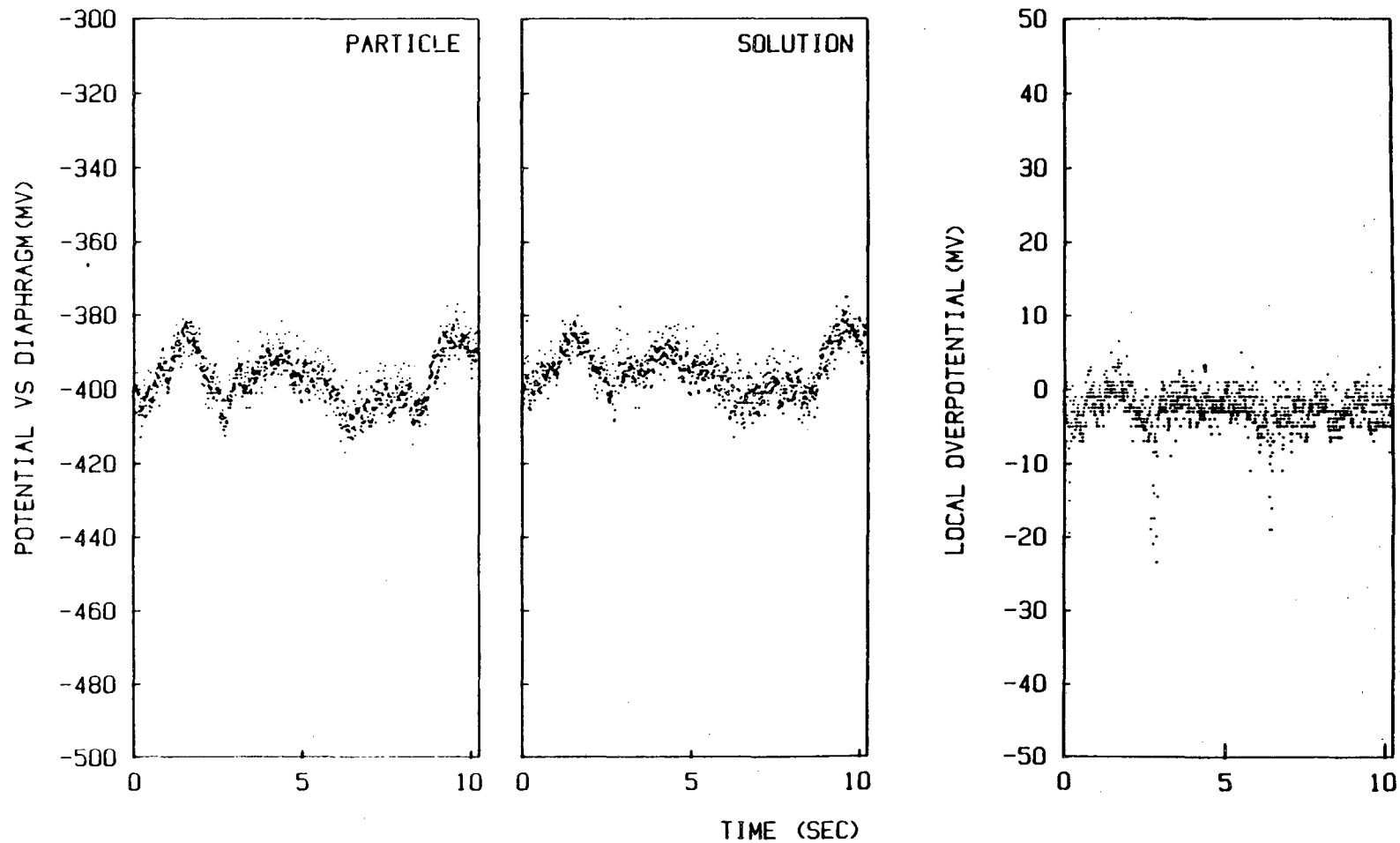
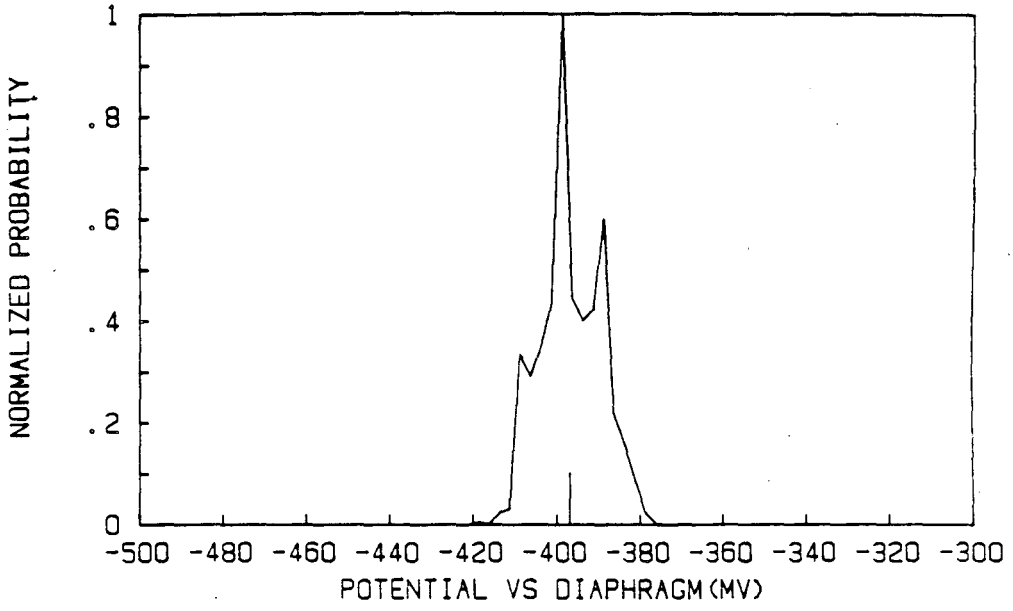
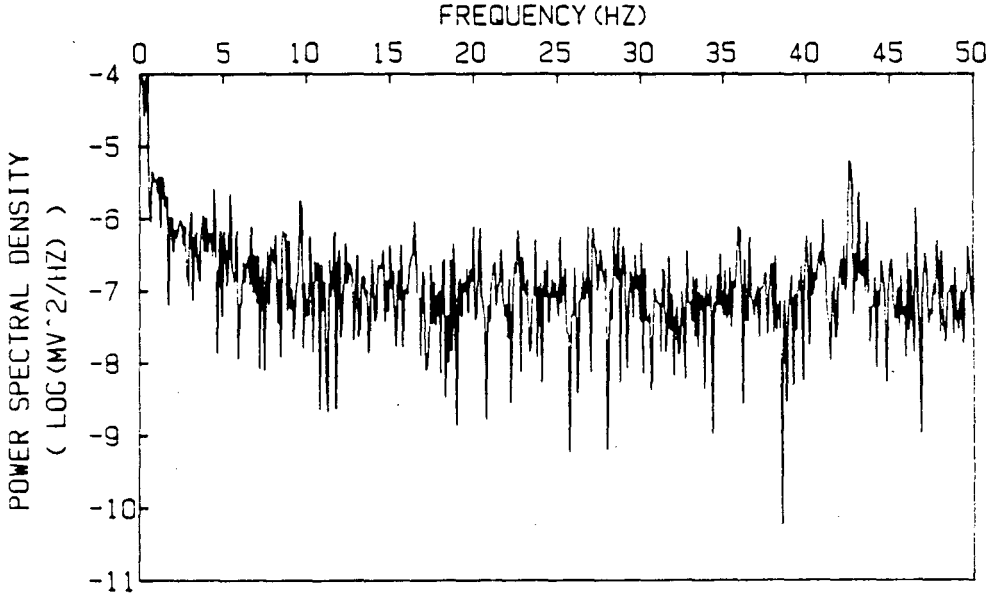


Fig. 10

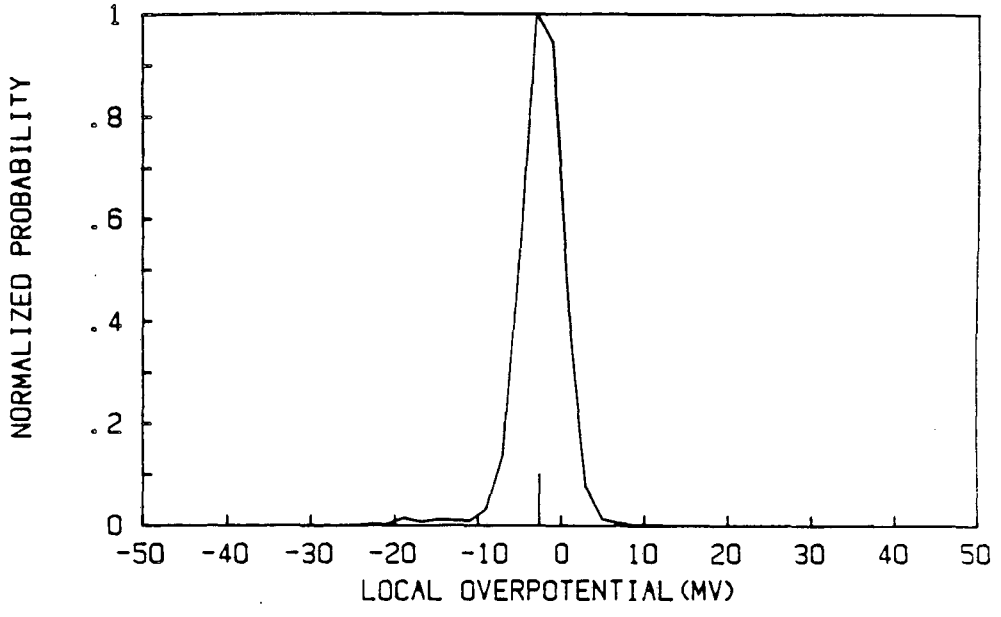
XBL 851-1032

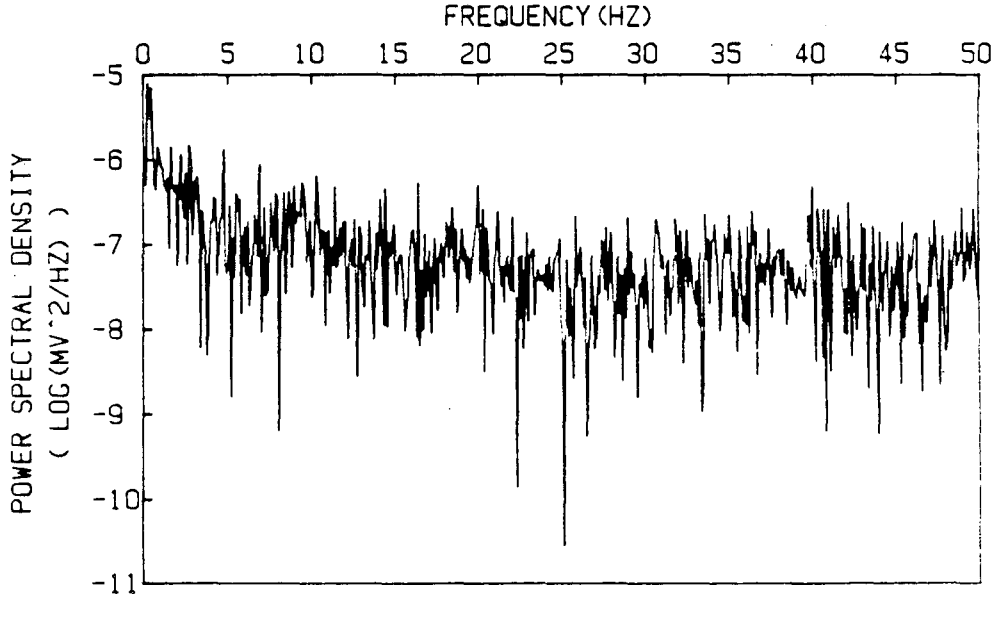




XBL 851-1030

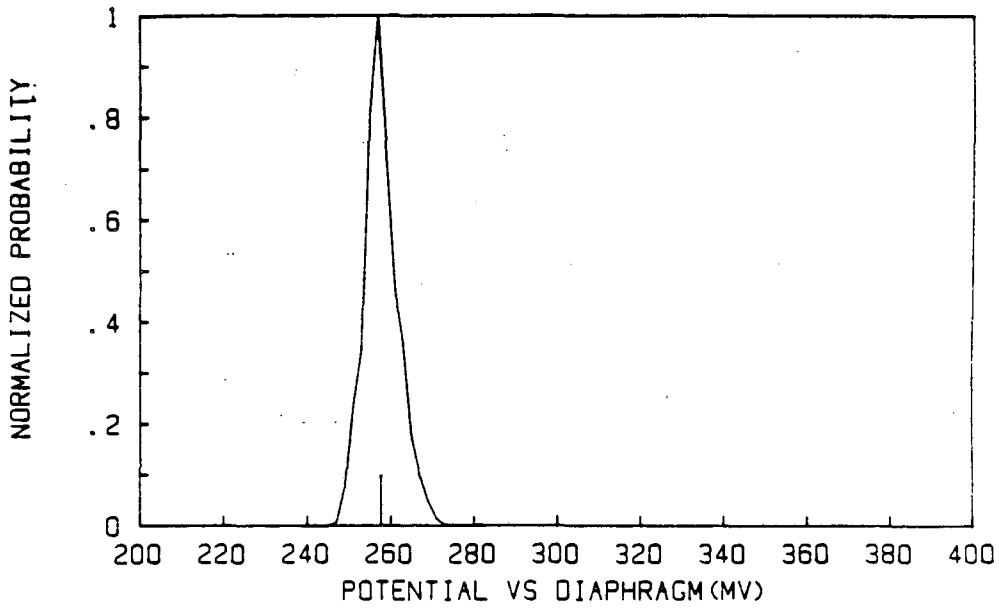
Fig. 11

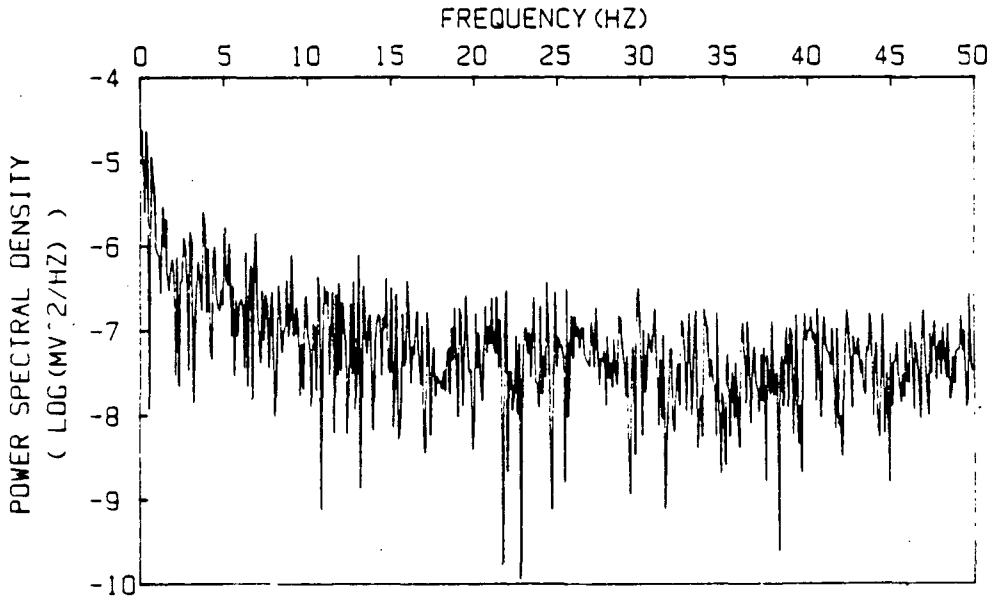




XBL 8510-4174

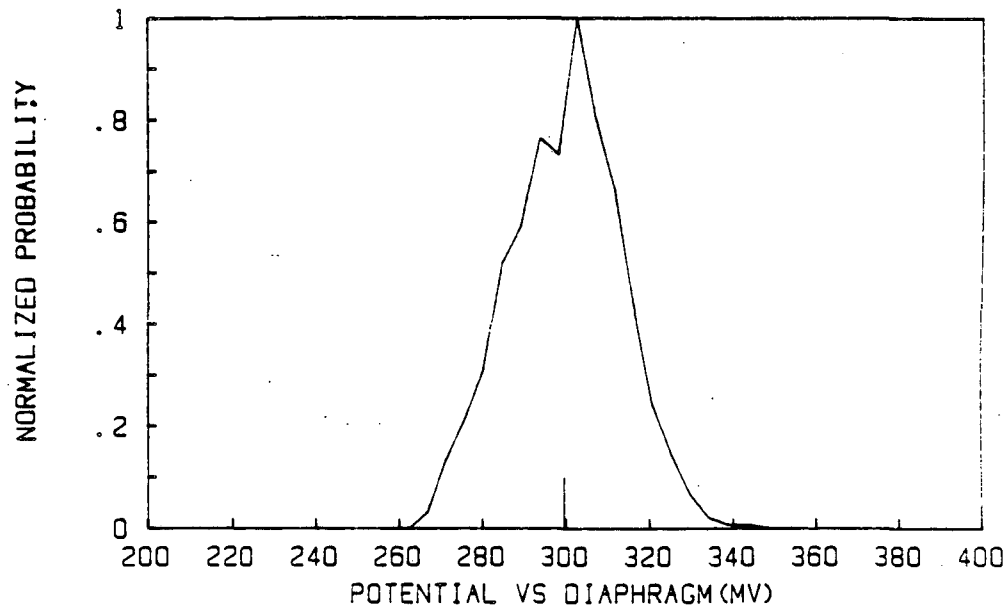
Fig. 12

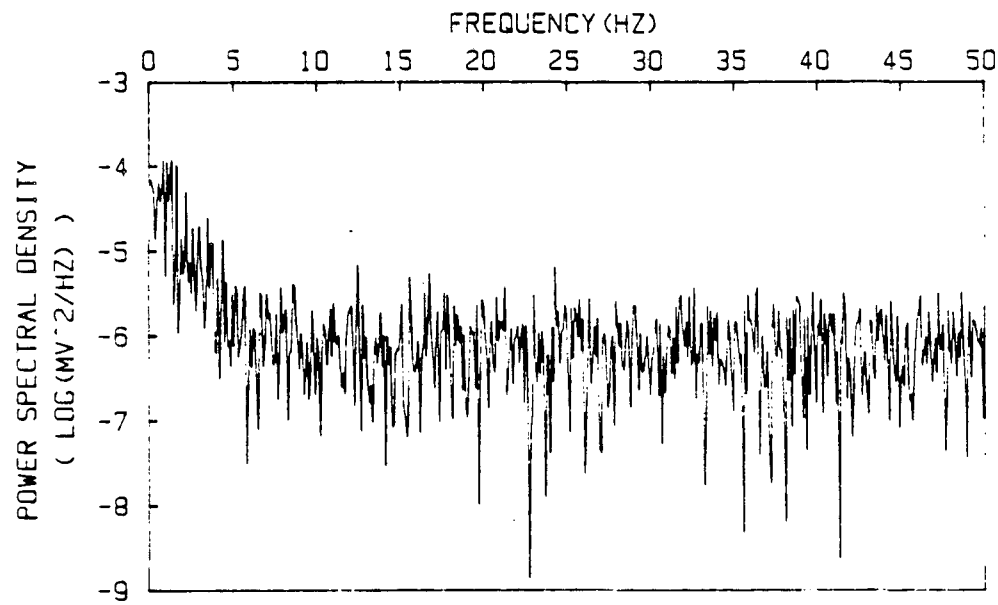




XBL 8510-4176

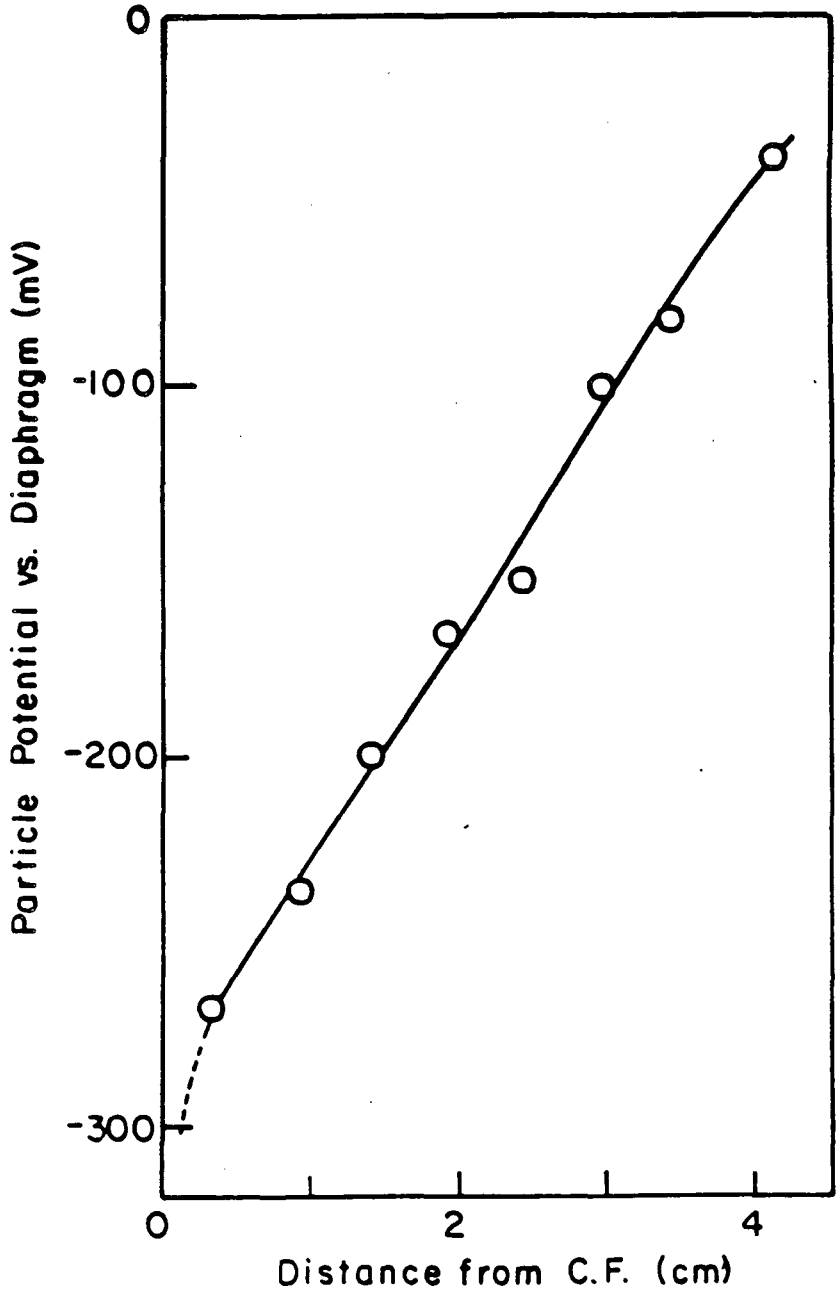
Fig. 13





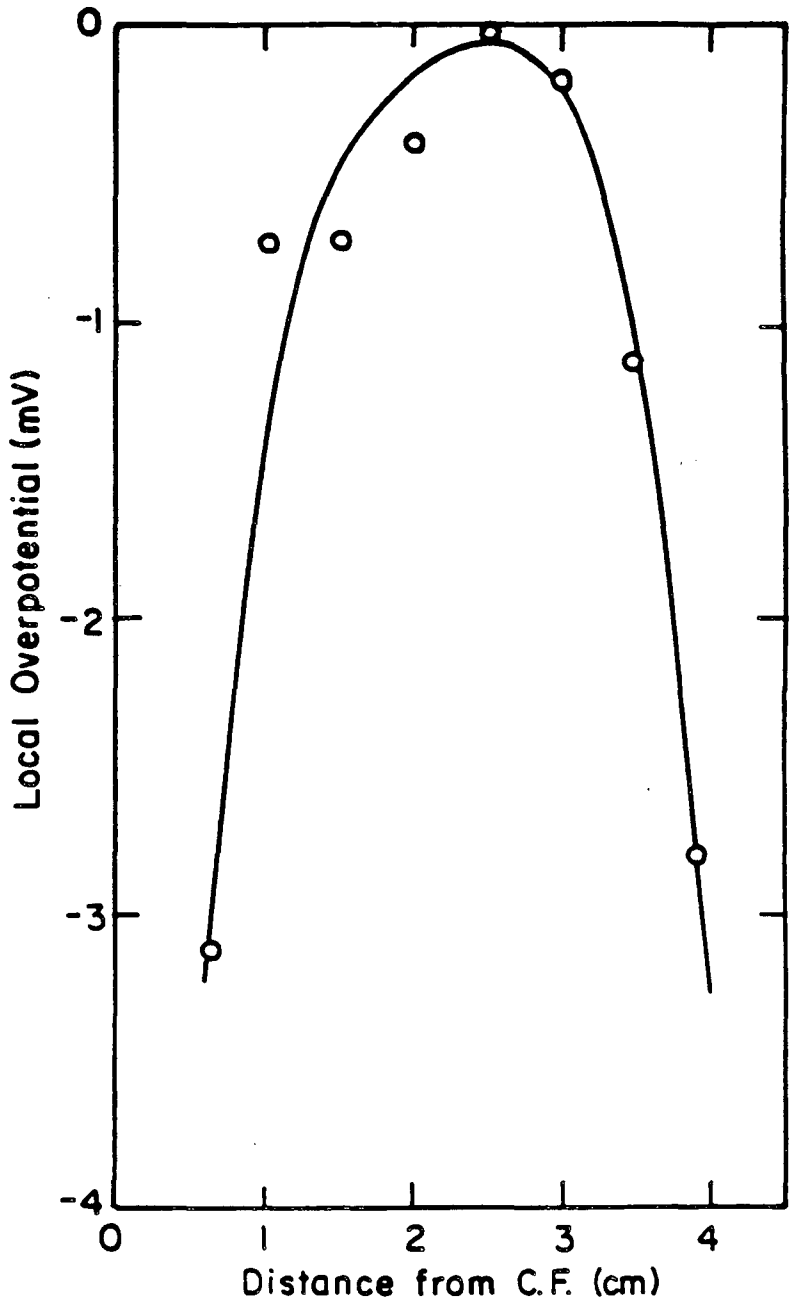
XBL 8510-4175

Fig. 14



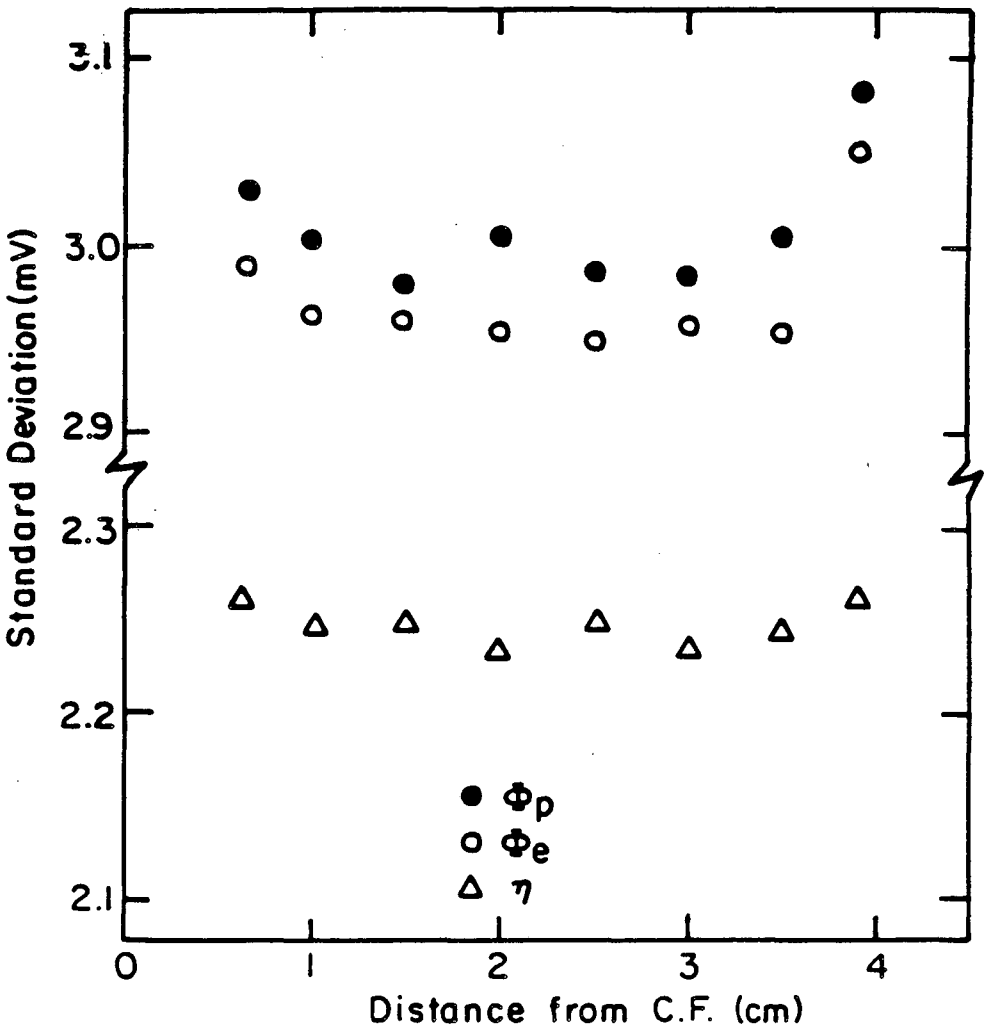
XBL 847-3273

Fig. 15



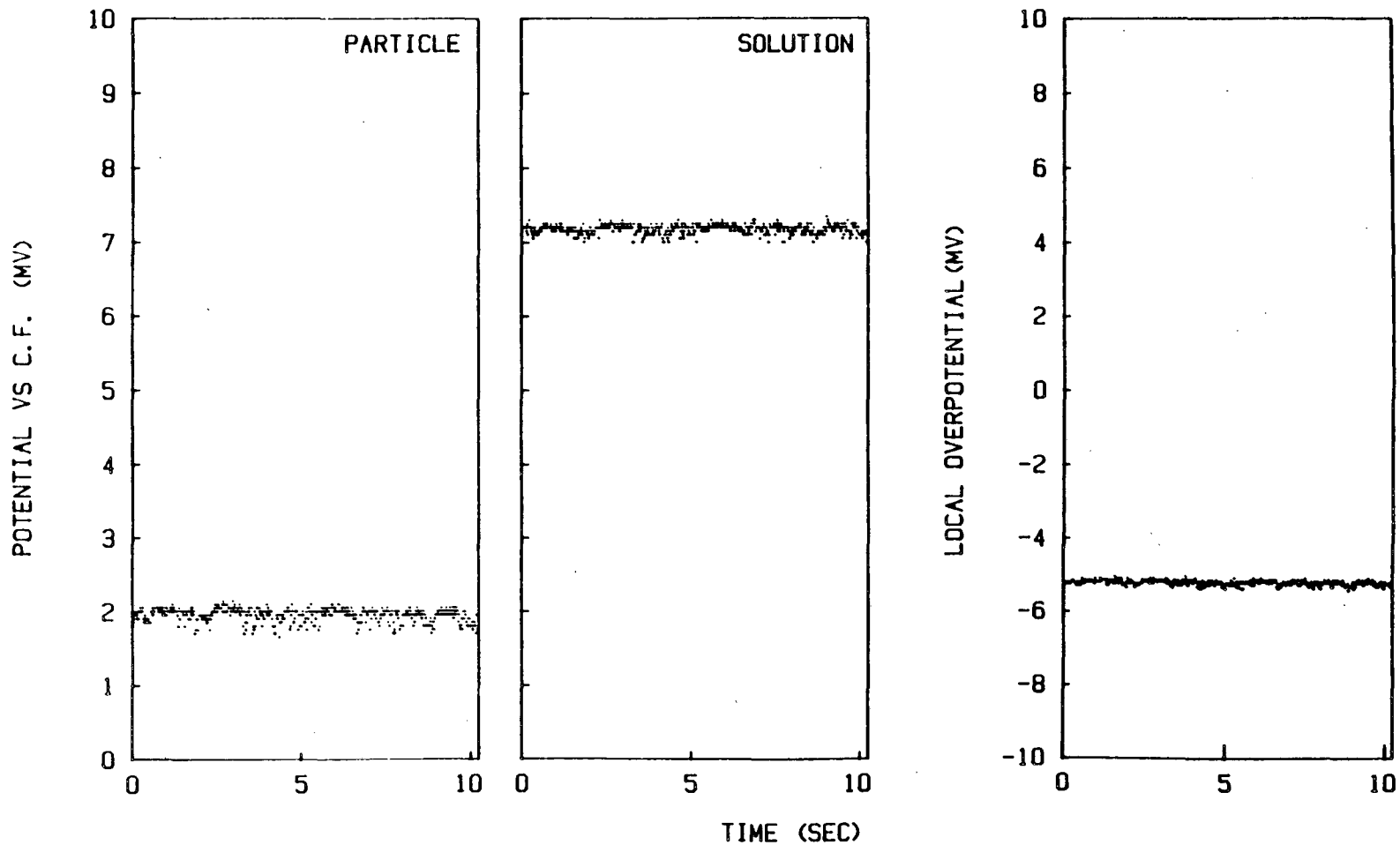
XBL 851-1031

Fig. 16



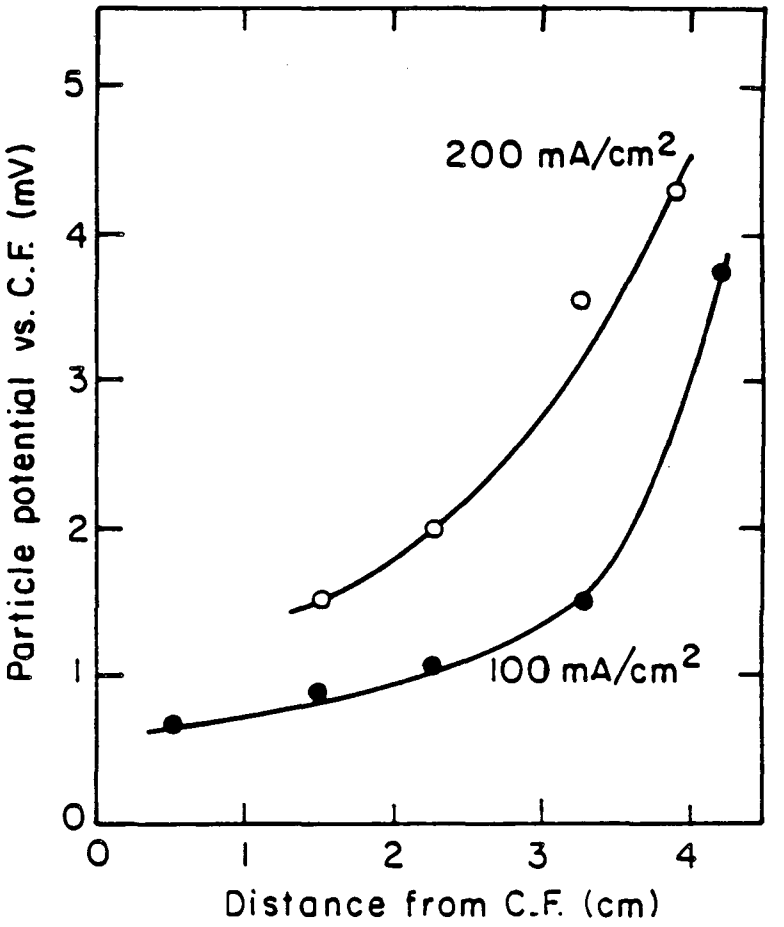
XBL 8510-4178

Fig. 17



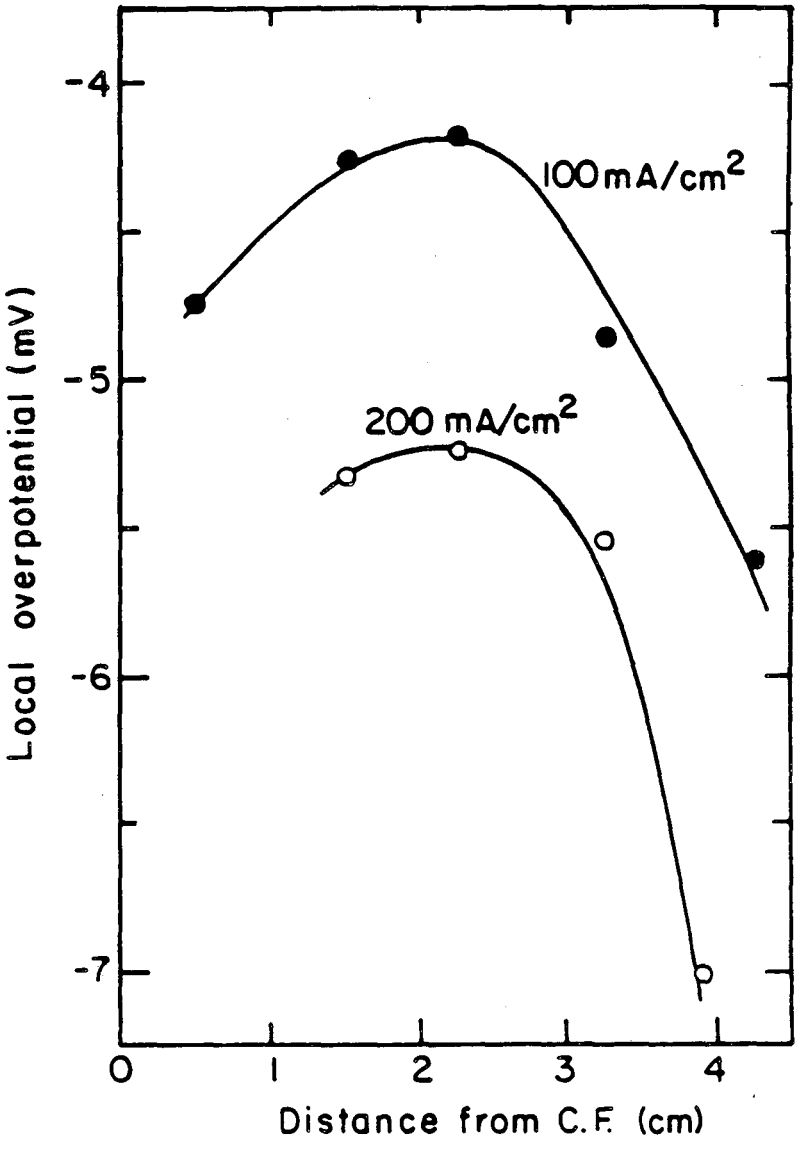
XBL 8510-4177

Fig. 18



XBL 8510-4179

Fig. 19a



XBL 8510-4166

Fig. 19b

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