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RESEARCH, DEVELOPMENT AND FABRICATION
OF LITHIUM SOLAR CELLS

Quarterly Report to January 1971

JPL Contract 952546

Jet Propulsion Laboratory
California Institute of Technology
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Pasadena, California 91103

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ABSTRACT

This quarter, more understanding and control of lithium cells resulted from studies of lithium concentrations at both the back surface and near the PN junction. Three hundred cells in Group C-13 are analyzed fully. A different sequence of fabrication steps was tried. The next 300 cells are now specified.

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1.0 Summary

This report continues studies on cells made with low temperature ($< 400^{\circ}\text{C}$) single-cycle, lithium diffusion schedules.

Measurements of concentration of lithium at the back surface showed that C_s changes with time, consisting of a build-up to a maximum value (above 10^{17} cm^{-3}) with gradual decrease at longer diffusion times. Using the estimated C_s values, theoretical lithium profiles were calculated. The calculated concentration near the PN junction was higher than those measured by the capacitance voltage (C-V) technique. The calculated concentration gradients were one-seventh of those measured by C-V methods. Both the concentration and its gradient were proportional to C_s .

Estimates of C_s obtained by extrapolating from C-V measured values of concentration and gradient near the PN junction, showed a decrease in C_s for longer diffusion times. This fact supported the trend observed in Shipment C-13, where, at longer times, the spread in values of V_{OC} , lithium concentration, and gradient became greater. The general conclusion was that the I-V characteristics were well controlled, with good cell output, but for longer diffusion times the lithium concentration gradient could have wider spread.

The work described has led to greater insight into the lithium distribution dependence on the surface conditions. The surface conditions could be changed by varying the method used to apply lithium. Vacuum evaporation of lithium shows promise, and another exhaustive test of this method is in progress. Shipment C-13 is summarized, and the succeeding lots (C-14, C-15) are described. It is felt that improved monitoring of cell properties is at hand, and that the control of cell fabrication processes has advanced to where the effects of subtle differences in lithium distribution can now be seen. Evaluation is continuing on the best method to scale up the fabrication steps. A different sequence of fabrication is planned for Shipments C-14 and C-15.

2.0 Introduction

The objective of this work is to develop high efficiency solar cells using lithium doping to improve cell output after irradiation. This contract continues work on controlling the cell fabrication procedures, to determine the major control steps and means for monitoring these steps. The procedures developed are combined to give closely controlled groups of cells which other organizations can irradiate, and analyze.

Exchange of information via JPL, concerning the control of the fabrication steps, and the results of irradiation analysis, allows specification of later cell groups.

The work described here builds on that already done (Ref.1). Thus, the emphasis is still on lithium diffusion temperatures below 400°C, with single-cycle diffusion rather than redistribution cycles. In addition, the key fabrication steps are being evaluated in terms of scaling-up to pilot production levels.

3.0 Technical

3.1 JPL Shipment C-13

This shipment was intended to extend the work described in Reference 1, Section 3.3.1, which described five separate temperature-time sequences (425°C - 90 min., 400°C - 90 min., 375°C - 180 min., 350°C - 300 min., and 325°C - 480 min.).

For C-13, five temperatures were chosen, namely 330°C, 340°C, 350°C, 360°C and 370°C. At each temperature, two separate diffusion time groups were used, as shown in Table 1. The times for the two 350°C diffusions were identical (300 min.) and were carried out at the beginning and end of the sequence, to check repeatability of the same sequence.

TABLE 1

Lithium Diffusion Schedules Used For Shipment C-13

(Lithium Paint-On)

Group	No. of Cells	Diffusion Temperature	Diffusion Time
13A	30	330 °C	180 min.
13B	30	330 °C	420 min.
13C	30	340 °C	180 min.
13D	30	340 °C	420 min.
13E	30	350 °C	300 min.
13F	30	350 °C	300 min.
13G	30	360 °C	180 min.
13H	30	360 °C	420 min.
13I	30	370 °C	240 min.
13J	30	370 °C	360 min.

For all ten groups, 30 cells were shipped. All cells fabricated were from the same CG ingot. Also, the slices all had the same surface finish (chemical-mechanical polish) and the same boron diffusion schedule. (BCl_3 with short (4 minute) tack-on time).

The slices were all boron diffused at once. By mistake, the BCl_3 temperature was 20°C high for the first 30% of the slices diffused (groups 13E, 13I, 13J). This led to a deeper PN junction but close examination of the final cells showed that this deeper junction did not have significant effect on any cell parameters except the obvious difference, a loss of 2-3mA in short circuit current. This loss was in short wavelength response, and agreed with earlier tests wherein the boron diffusion schedule was varied intentionally. The two groups of cells processed at 350°C (E and F) were diffused at these two boron temperatures, 1050°C and 1070°C and later results show that apart from I_{sc} variations, they are fairly well matched. Therefore, in comparing these ten groups, the three groups with deeper junctions, (13E, 13I, 13J) had the measured I_{sc} adjusted upwards by 2.5mA.

At each lithium diffusion temperature, the slices had the lithium source painted on, and they were placed on a two-part boat. This allowed simultaneous lithium application, and similar initial conditions at the back silicon surface, where the lithium was applied. The shorter time run cells were removed, leaving the other part of the boat for the longer diffusion time. The successive cell batches were kept separate and after cells were fabricated, the I-V values, and the spreads of the values, were analyzed to determine if the differences in cell behavior could be correlated with the batch.

3.1.1 C-13 Cell Measurements

NOTE: All I-V measurements refer to AMO, 140 mW/cm², cell at 28°C.

Figure 1 shows average values for P_{max} , V_{oc} , I_{sc} and zero bias capacitance, for the ten 30-cell groups. The P_{max} values are high and fairly closely grouped. I_{sc} generally varies out-of-phase with V_{oc} and the capacitance. The out-of-phase behavior of I_{sc} and V_{oc} explains why the P_{max} variations are small.

Figure 2 shows the total spread of the values for P_{max} , V_{oc} and capacitance, in this case plotted as a function of increasing diffusion time. Again the P_{max} values have fairly small spread. V_{oc} has reasonably small spread also, with a greater range of measured values at the longer times. The capacitance values show the same trend to greater spread at the longer times.

Figure 3 shows the wide spread in measured concentration gradients, revealing that the small spread in I-V characteristics may be accompanied by larger spreads in parameters associated with the lithium concentration or with the concentration gradient.

Figure 4 shows the cumulative percentage plot of P_{max} . The average for all 300 cells in C-13 is plotted, all groups falling between the limits shown for separate groups. Shipment C-12 is plotted for comparison.

Figure 5 reveals close correlation between the V_{oc} and the lithium concentration and gradient. For the shorter times, the grouping is tighter, and in addition, the values of V_{oc} and the lithium parameters are higher. It should be noted that the V_{oc} values are generally high even for the cells with less lithium, but that greater resolution of the underlying correlations is now possible.

In Figure 6, plotted for 100 cells, 10 in each of 10 groups, it can be seen that V_{oc} is approximately proportional to the logarithm of the lithium concentration with an average slope near the expected value, 0.026 volt. Again, it should be noted that the total range of V_{oc} values is around 5%, whereas the total range of concentration values is 400%.

Table 2 shows the surface concentration values calculated by combining the lithium concentration at the junction, and the lithium gradient assumed to be spread over 20 μm from the junction, and extrapolating back to the back surface, assuming a complementary error function distribution, indicative of diffusion from an infinite source. In general, C_s falls off at larger diffusion times.

3.2 Lithium Distribution

The work described in previous reports included some measured lithium properties (see Figures 3 through 6, Reference 1) and the distributions shown are now better understood, and help explain some of the results obtained for Shipment C-13.

Theoretically, assuming the lithium follows a complementary error function distribution both the lithium concentration at any plane in the cell, and the gradient at that plane, are proportional to the surface concentration (C_s) of lithium. However, the calculated values are widely different from those measured near the junction by the C-V technique. The measured concentration is much less, and the measured gradient is much greater (approximately seven times). This is consistent with movement of the lithium at the diffusing front into the sink formed by the PN junction at the front surface.

Some additional insight was obtained by measuring the value of lithium surface concentration (C_s) at the back surface as a function of time. For the paint-on source, Figure 7 shows that there is fairly rapid increase of C_s with time, faster at higher temperatures. Even so, the maximum value may require around one hour diffusion, and there is a tendency (noted also in Table 2) for C_s to decrease at longer times. For a series of five increasing times at a fixed temperature of 330°C, using the measured values of C_s , Figure 8 plots the theoretical lithium profile, and also shows the values at the junction estimated from capacitance values. There is fair agreement, in that the three shorter times do not show any added lithium near the junction, and the capacitance values confirm this.

TABLE 2

Surface Concentration of Lithium for C-13 Groups

Combined the lithium concentration at the PN junction and the measured lithium concentration gradient near the junction, assumed to be spread over 20 μm .

Also assumed complementary error function distribution.

Group	T(°C)	t(min)	Calculated C_s (cm^{-3})
13A	330	180	1.3×10^{17}
13C	340	180	1.7×10^{17}
13G	360	180	1.6×10^{17}
13I	370	240	0.95×10^{17}
13E	350	300	1.2×10^{17}
13F	350	300	1.2×10^{17}
13J	370	360	0.75×10^{17}
13B	330	420	0.7×10^{17}
13D	340	420	0.5×10^{17}
13H	360	420	0.65×10^{17}

3.3 Lithium Introduction

As can be seen above, the lithium concentration and gradient near the junction are the keys to the cell performance before and after irradiation. C-13 showed that the paint-on source could give fair consistency, but the trend was for reduced surface concentration (with corresponding lower values for concentration near the junction) at longer times. This is consistent with a gradually depleting source. Another possibility was that lithium leaked to the front of the cell and entered the front surface, in increasing amounts for the longer time. However, this would tend to increase the concentration and decrease the concentration gradient near the junction at longer times, both opposite to the observed trend.

A few tests showed that use of a more concentrated source, such as that obtained from evaporated lithium metal, could reduce the spread in lithium parameters, even for longer diffusion times.

This led to renewed efforts to control the techniques used for lithium evaporation. Compared to earlier work, several factors are more favorable. First, the amount of lithium to be introduced is lower, and the diffusion temperatures are lower. Thus, there is less chance of loss of lithium in the vacuum enclosure or to the front surface of the cell. Also, a water cooled substrate was used, and the cells were kept in an inert atmosphere and transferred faster to the diffusion furnace. In addition, as discussed below, a change in the sequence of fabrication allowed the front P+ surface to be covered by a protective boron skin during lithium application and diffusion. The front contacts and coating could be applied after the lithium cycle.

3.4 Fabrication Sequence

For the present tests, the surface finish of the slices was kept constant. This meant that the front surface was mechanically-chemically polished, and the back side was of rough finish (as sawn) but etched lightly.

Also, the boron diffusion methods developed by Centralab last year (reduced tack-on cycles with BCl_3) were maintained because they gave well controlled cells, of good output with both oxygen-rich and oxygen-lean silicon, and thus allowed the variables of the lithium introduction to be examined in more detail. The search for greater consistency of cell fabrication continued. The various fabrication steps interact, and their order of performance is important.

For example, previously the front surface contact and coating were in place before the lithium was introduced, thus allowing a more severe sintering cycle to be used. However, there was the chance of attack of the contact and coating by the lithium during its application and diffusion. In the next group of cells, a larger scale test will be made of the sequence where the front surface contact and coating are applied after lithium diffusion. Preliminary tests have shown good consistency of I-V properties, and adequate adhesion with the use of moderate sinter cycles, below the temperature used for lithium diffusion.

Also, as mentioned above, it is possible to leave a protective layer on the P+ layer through the lithium diffusion, a factor favorable to use of the lithium metal evaporation process.

3.5 Other Topics

Previous work has discussed the possible advantages of slightly more complex structures. For example, N+ layers (with doping levels considerably greater than those obtained from the lithium diffusion) have been applied to the back surface either by phosphorus diffusion or from alloying with antimony alloys. These layers have a dual role, to reduce the contact resistance at the back surface, and to maintain this low resistance even when the lithium becomes depleted after irradiation. In practice, this depletion condition is only severe after very high fluence levels, well above the target fluences being considered in the present work. For this reason, and also because the lithium doping, when well controlled, can provide satisfactorily low resistance, the present cells do not have an additional N+ layer.

Also, the possibility of the use of an N+ layer at the front surface, extending slightly deeper than the P+ layer, has been discussed as a guard against serious depletion of donors near the PN junction when lithium is removed to interact with the recombination centers. Again, this front N+ layer should only be needed after very high fluences, unless it can be used to alter the lithium distribution near the front surface during diffusion, and thereby improve the recovery characteristics. Some tests on this latter possibility are in progress.

Along related lines, some lower resistivity Lopex silicon will be included in the next shipment of cells, to evaluate the effect of increasing the background donors five-fold.

3.6 Next Shipments

The next two shipments have been specified.

Shipment C-14

Two different forms of silicon, oxygen-rich (OR) and oxygen-lean (OL) will be used. The OL silicon will have medium resistivity, around 15 ohm-cm. The OR silicon will be about 30 ohm-cm.

Two different lithium diffusion cycles, still in the same range as the last three Shipments C-11, C-12 and C-13, will be used. These schedules are 375°C - 180 min., and 350°C - 300 min.

Shipment C-15

In this lot, three different silicon ingots will be used (OL 15 ohm-cm, OL 75 ohm-cm, OR 30 ohm-cm) all diffused for the same schedule 350°C - 240 min. Each group of the three ingots will be split, with lithium being painted-on half the groups, and lithium metal being evaporated on the other half. This will provide a good comparison of the control possible with these two lithium techniques. The comparison between the two OL ingots, with five-fold doping difference, will be noted. In addition, a seventh group will use OR silicon as above, and evaporated lithium, with a diffusion schedule 350°C - 480 min., to study the effects of the longer time with the more concentrated lithium source.

4.0 Conclusions

This quarter's work has further explored the advantages seen earlier in the use of lower temperature, single time diffusions. More quantitative analysis methods have been combined with good control of the I-V properties before irradiation. The feedback from irradiation work will be used to lead future work towards even better cell control and characterization. The evaluation procedures already developed will prove very useful when comparing various fabrication sequences for the expansion to pilot-scale rates of fabrication.

Work for the next quarter will continue along the lines described in this report.

5.0 New Technology

The work described here has applied already existing technology, and is not considered to include new technology.

6.0 References

1. "Research, Development and Fabrication of Lithium Solar Cells". Final Report, Part 1, November 23, 1970 - Centralab Semiconductor. JPL Contract 952546.

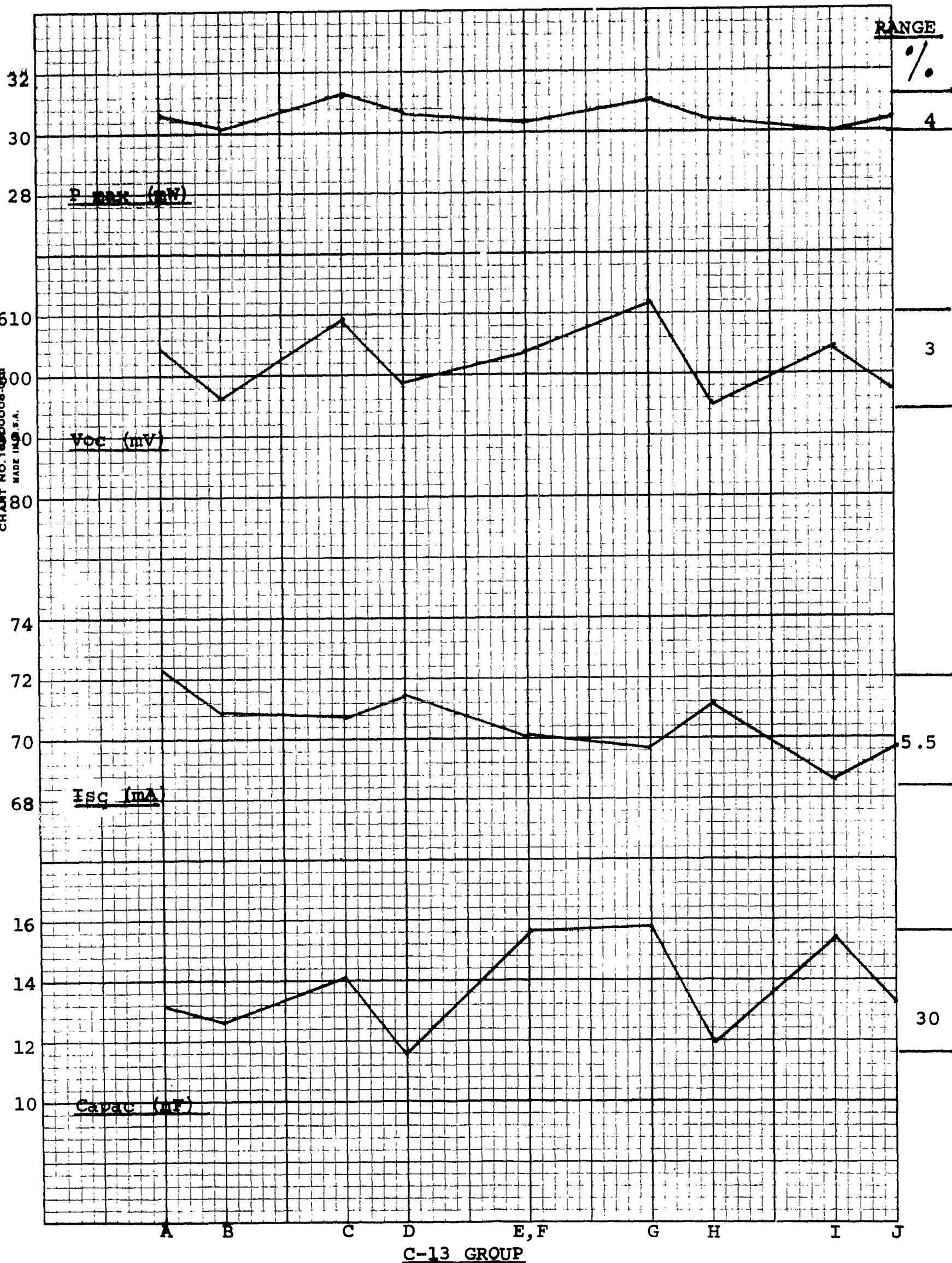


Fig. 1 Average values for Pmax, Voc, Isc and capacitance, for the ten C-13 groups.

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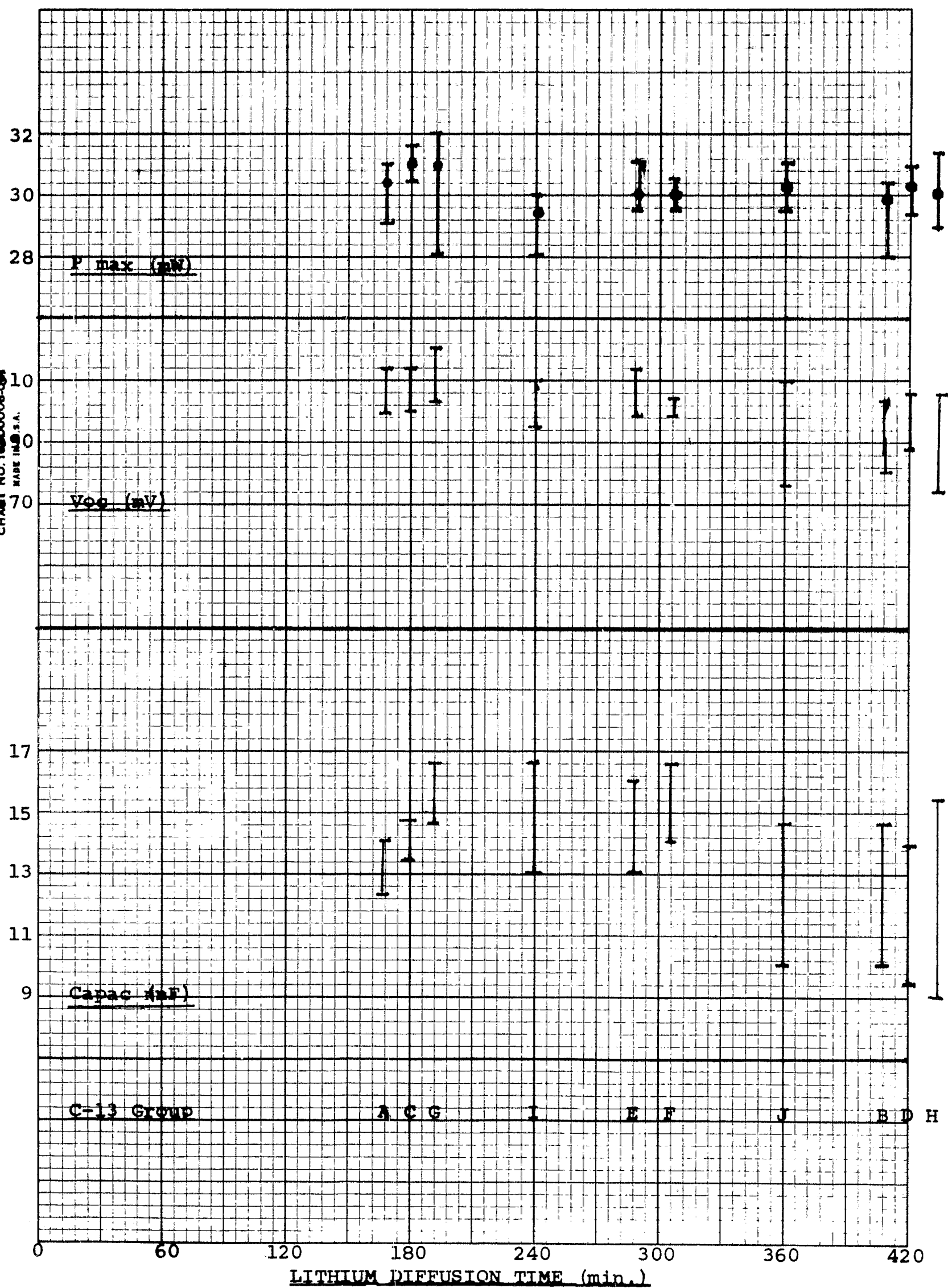


Fig. 2 Average values and spread for Pmax, Voc, and capacitance, for the C-13 groups, plotted as a function of diffusion time.

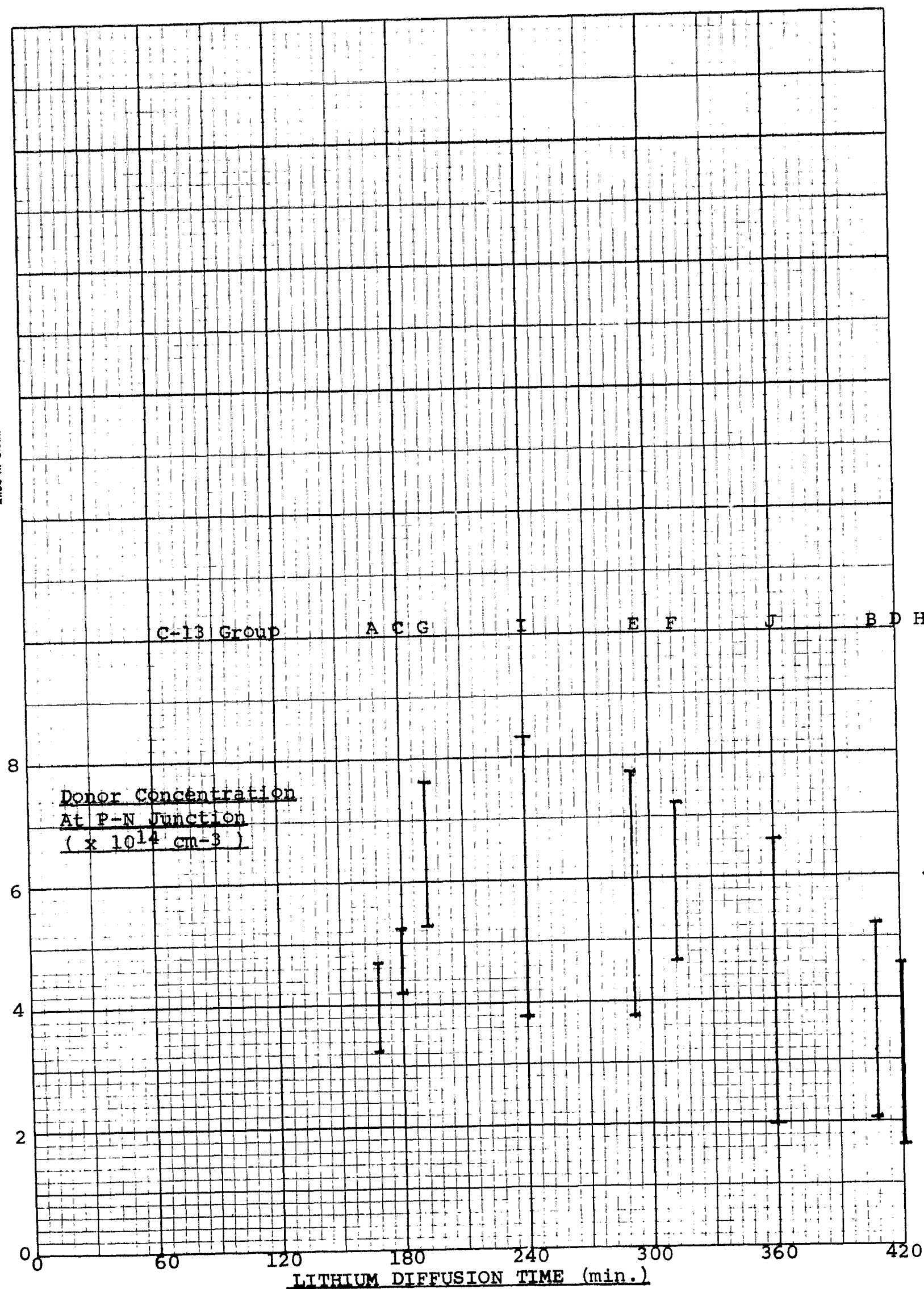


Fig. 3 Average values and spread of donor concentration gradient at the PN junction, for the ten C-13 groups, plotted as a function of diffusion time

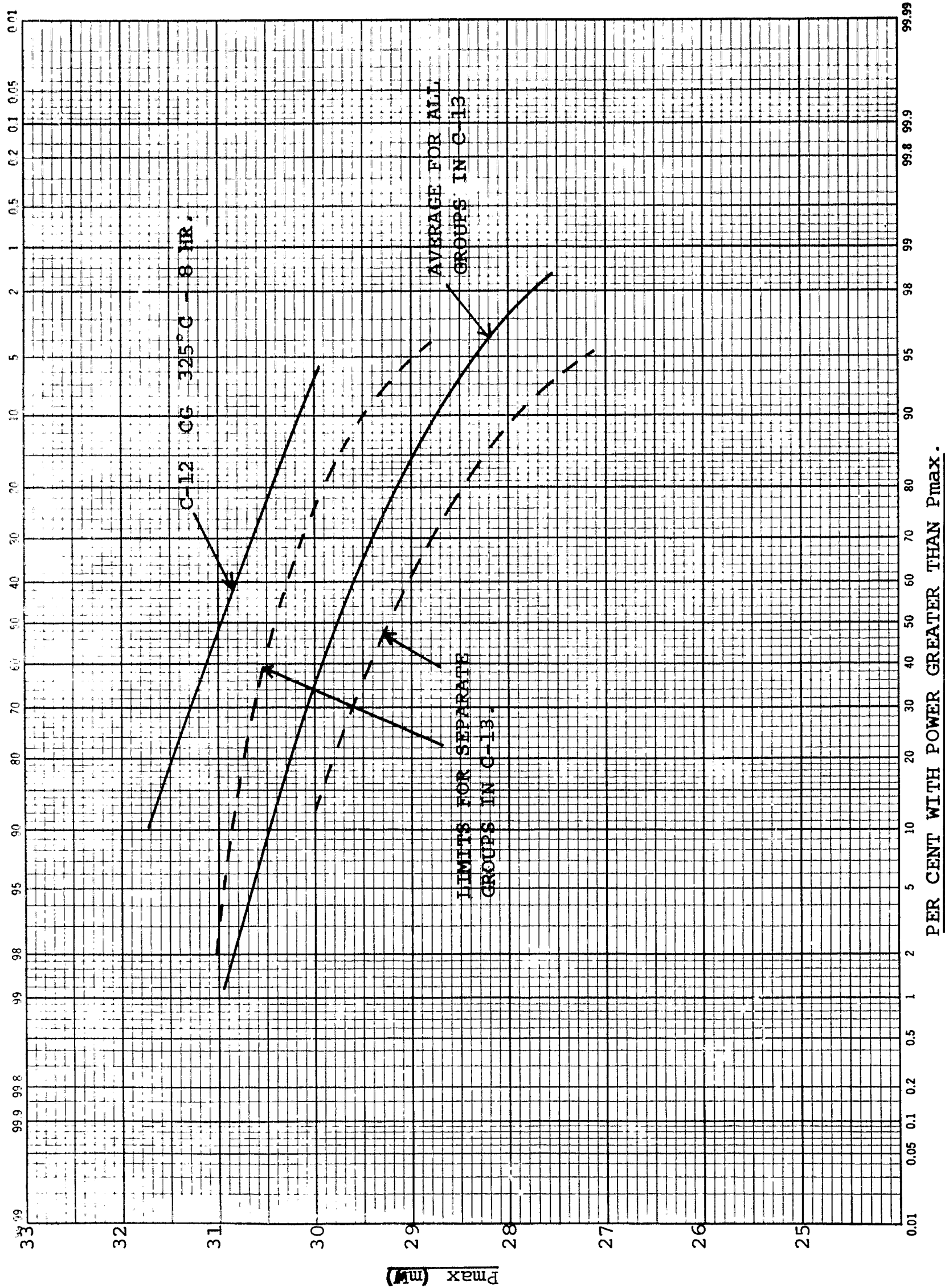


Fig. 4 Cumulative P_{max} distribution for total and extreme groups

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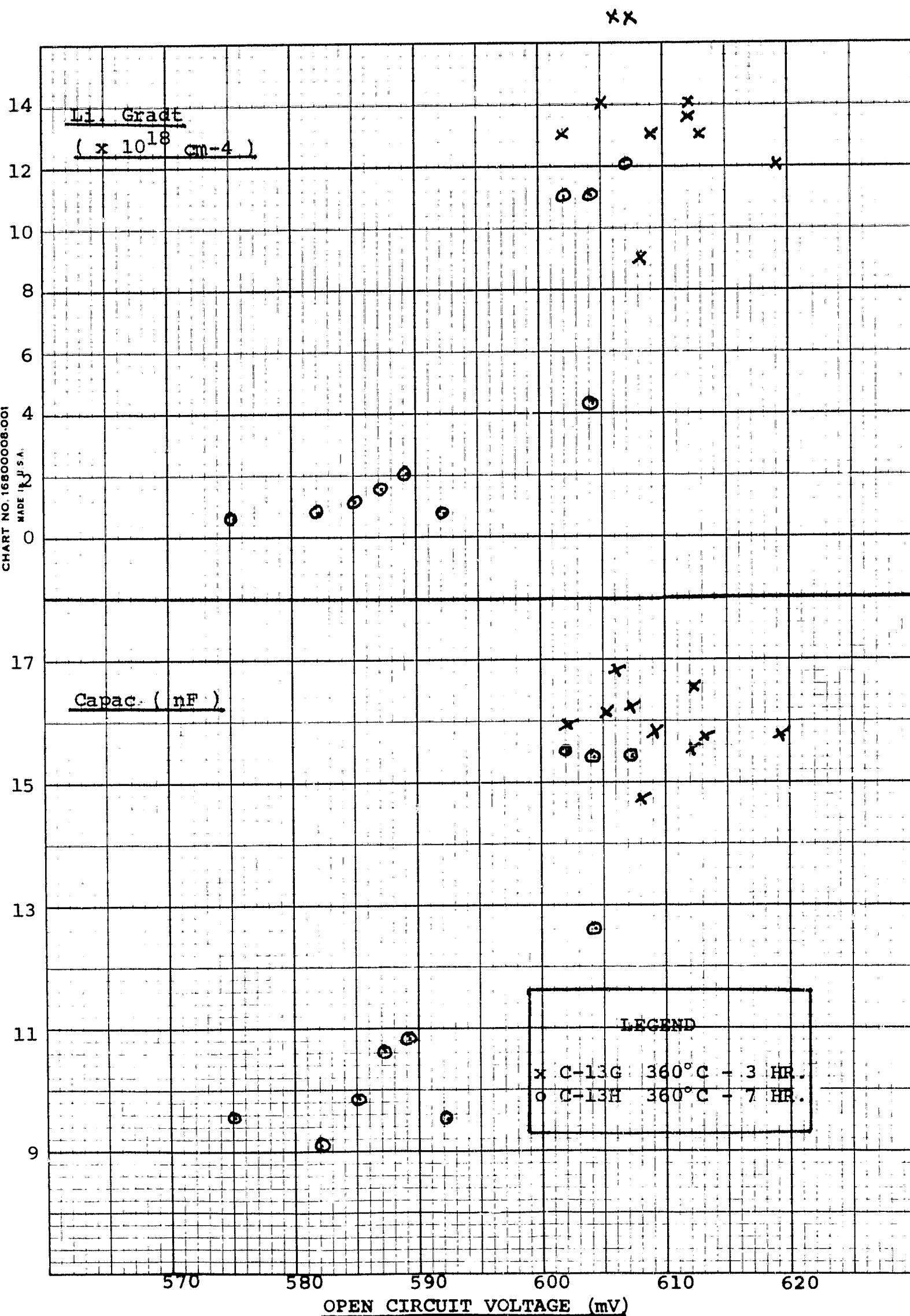
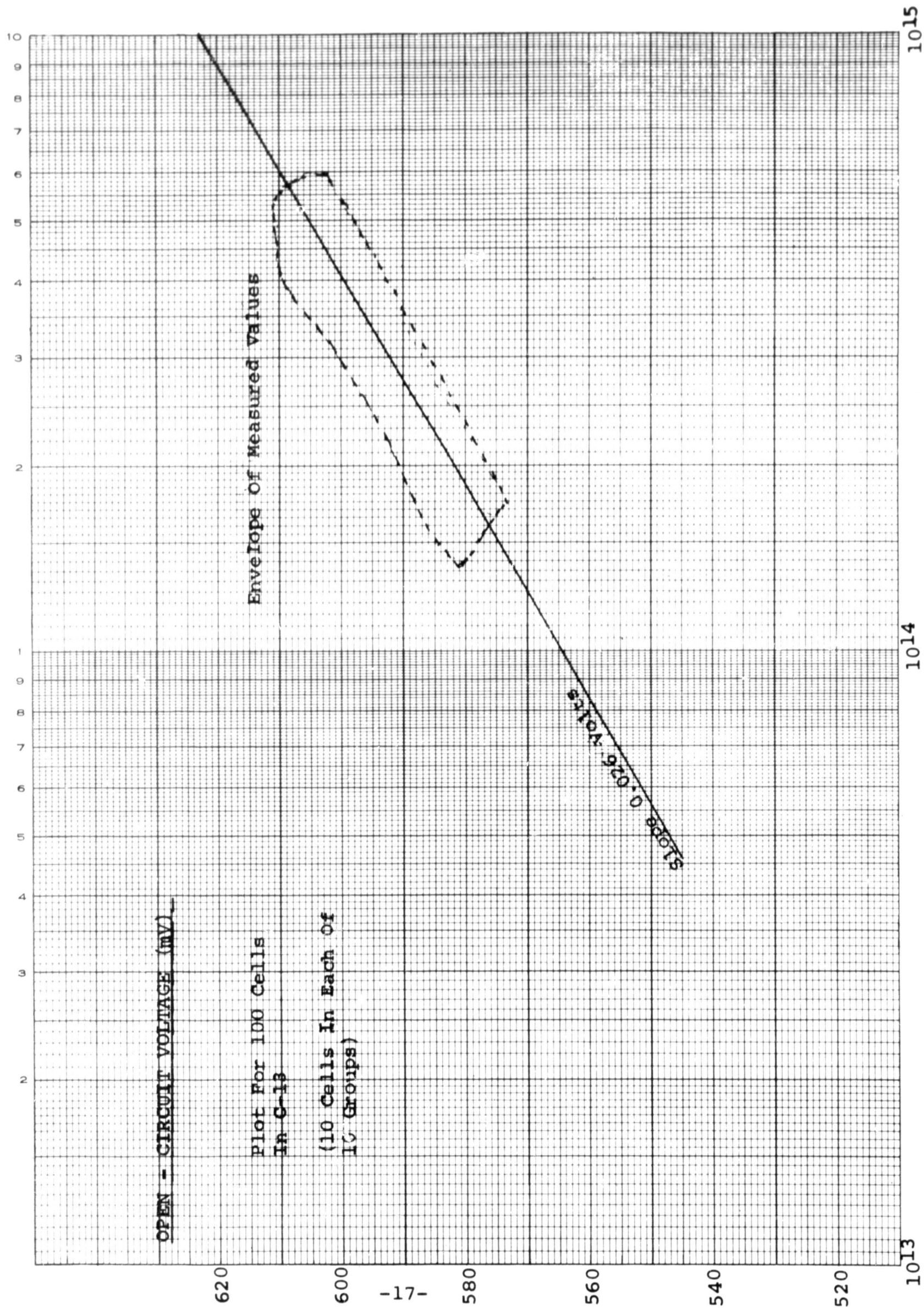


Fig. 5 Voc plotted versus capacitance and lithium concentration gradient near the junction for two 10-cell groups in C-13.



LITHIUM CONCENTRATION AT P-N JUNCTION (cm-3)

Fig. 6 Voc plotted against logarithm of the donor concentration for 100 cells, 10 in each C-13 groups.

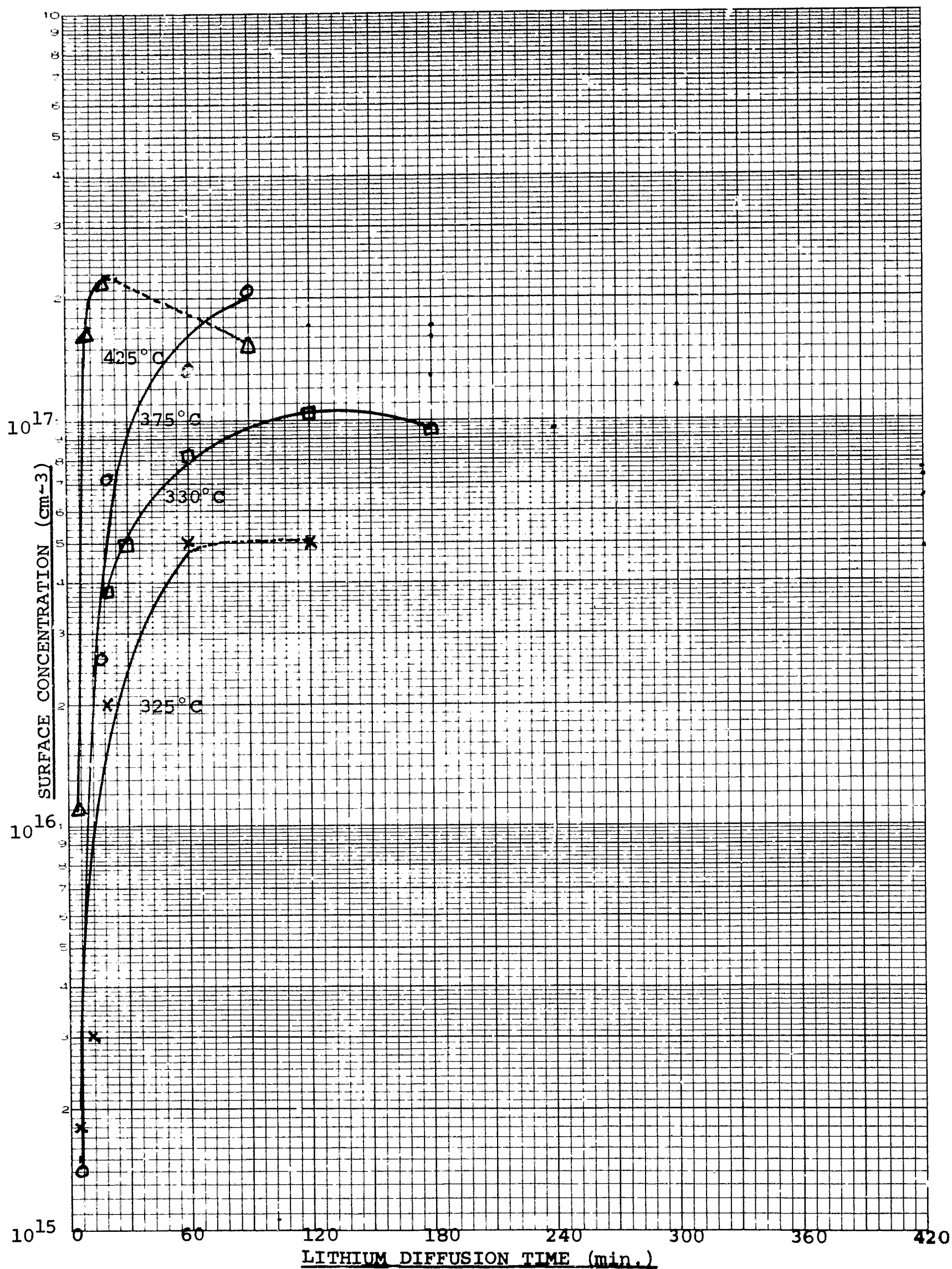


Fig. 7 Build-up of surface concentration of lithium, for increasing time at various temperatures.

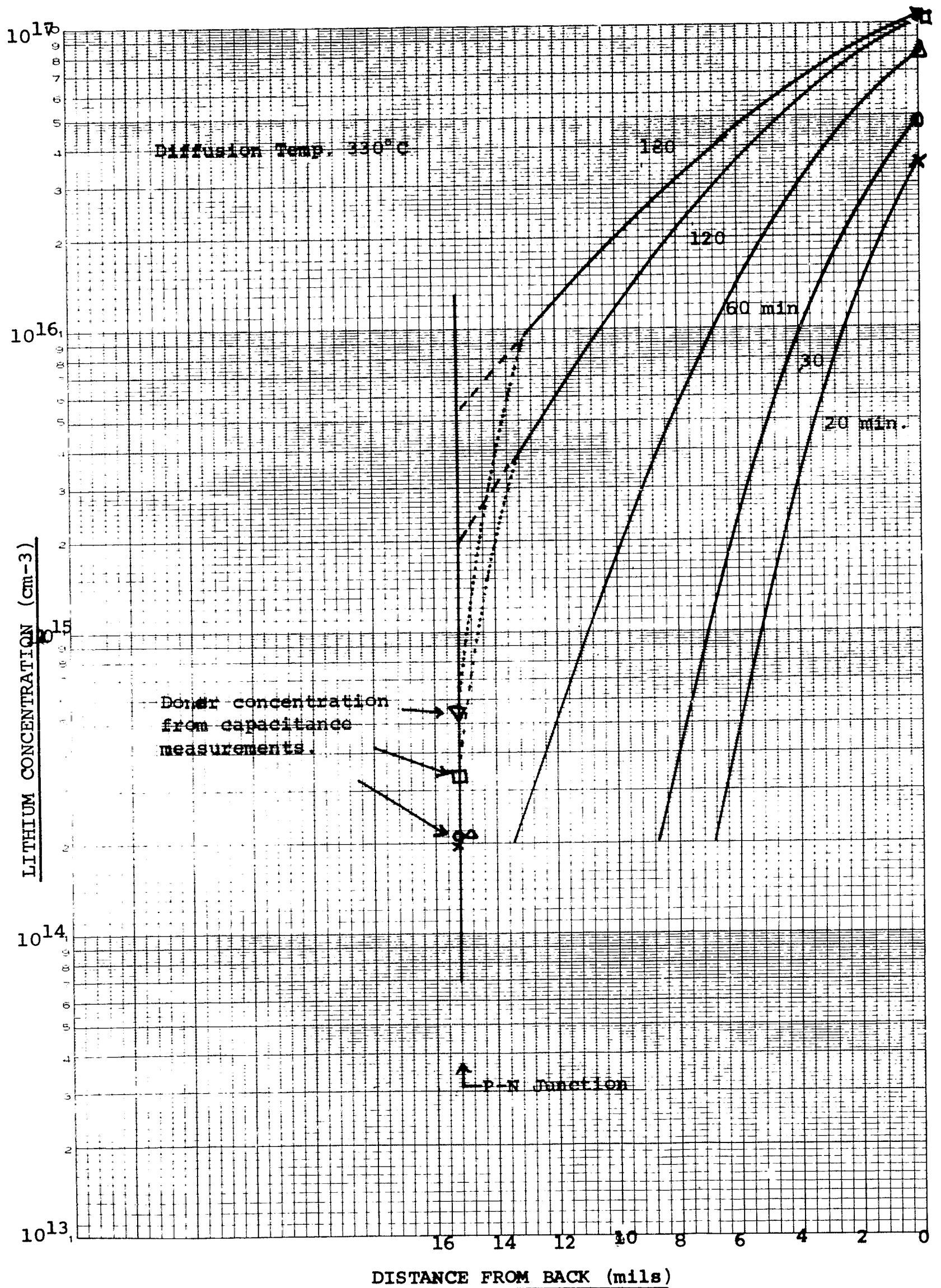


Fig. 8 Changes in lithium concentration profile, and the values measured at the PN junction, as the diffusion time at 330°C was increased.