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Development of Lithium Diffused Radiation Resistant Solar Cells

Report No. 11

Final Report

by

P. Payne

20 March 1969

JPL Contract No. JPL 952247

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, as sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

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(PAGES) — (CODE)

CR-105318 (NASA CR OR TMX OR AD NUMBER) — 03 (CATEGORY)

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ABSTRACT

Six hundred lithium doped P/N solar cells have been fabricated and delivered to JPL for radiation testing and analysis by other laboratories. Statistical analysis of the cell outputs was performed for each lot of cells delivered. Ten lots of cells were delivered and each lot of sixty cells were fabricated using the same material and diffusion parameters so that large number statistics could be used in evaluating radiation recovery characteristics. Significant improvements in cell efficiencies were made during the past year and particularly high efficiencies were obtained with crucible grown lithium cells. The average output ranged from 26.0 mW for the first lot to 29.0 mW for the tenth lot. Improvements were also made in cell uniformity as shown by the narrow maximum power distributions shown for some of the lots.

In addition to fabricating the 600 cells for delivery to JPL, experiments were designed to evaluate and improve processing techniques as well as cell outputs. Lithium evaporations and various lithium diffusion parameters were investigated. Boron diffusions were also studied and by making a process modification the uniformity of lithium cell output was improved. Investigation of sintering lithium cells showed that in some cases sintering can cause significant improvements in cell output.

Measurements over a 2-1/2 year storage period show that changes in lithium cells do occur, although in most cases the losses were less than 2%. In general the crucible grown lithium cells showed improvements after storage. The float zone cells diffused at 425°C varied; some showed improvements and others showed degradation. The float zone cells diffused at 350°C had slightly lower characteristics after one year of storage and recent measurements made after two years of storage showed slight improvement. Cells which were fabricated early in this contract period and re-measured for stability showed no changes in the case of the crucible grown

lithium cells; however, the Mon-x and float zone cells fabricated for Lots 3 and 4 approximately six months ago showed short circuit current losses of 2.5-4.0 mA.

TABLE OF CONTRENTS

Section	Description	Page
1.0	Introduction	1
2.0	Technical Discussion	2
2.1	Procedure for Fabrication of Lithium Doped Solar Cells	2
2.2	Experimental Studies	2
2.3	Cells Delivered to JPL	26
3.0	Conclusions	61
4.0	Recommendations	62
5.0	New Technology	63

List of Illustrations

Figure	Description	Page
1	Average Cell Outputs from Ten Lithium Diffusions	8
2	I-V Curves Before and After Sintering Lithium Diffused P/N Cells	16
3	I-V Curves of an Unsintered Lot of Lithium Diffused P/N Cells	17
4	I-V Curves after Sintering of the Lot of Lithium Diffused P/N Cells Shown in Figure 3	18
5	I-V Curves Before and After Sintering of a Low Output Lithium Diffused P/N Cell	20
6	I-V Curves Before and After Sintering of an Average Output Lithium Diffused P/N Cell	21
7	Concentration Profiles	27
8	Maximum Power Distribution of Lithium Cells Fabricated for the First Shipment Lot	28
9	Short Circuit Current Distribution of Lithium Cells Fabricated for the First Shipment Lot	30
10	Maximum Power Distribution of Lithium Cells Fabricated for the Second Shipment Lot	31
11	Short Circuit Current Distribution of Lithium Cells Fabricated for the Second Shipment Lot	32
12	Maximum Power Distribution of Lithium Cells Fabricated for the Third and Fourth Lots	34
13	Short Circuit Distribution of Lithium Cells Fabricated for the Third and Fourth Lots	35
14	Maximum Power Distribution of Lithium Cells Fabricated for the Fifth Lot	37
15	Short Circuit Current Distribution of Lithium Cells Fabricated for the Fifth Lot	38
16	Maximum Power Distribution of Lithium Cells Fabricated for the Sixth Lot	39
17	Short Circuit Current Distribution of Lithium Cells Fabricated for the Sixth Lot	40
18	Maximum Power Distribution of Lithium Cells Fabricated for the Seventh Lot	42
19	Short Circuit Current Distribution of Lithium Cells Fabricated for the Seventh Lot	43

Figure	Description	Page
20	Maximum Power Distribution of Lithium Cells Fabricated for the Eight Lot	45
21	Short Circuit Current Distribution of Lithium Cells Fabricated for the Eighth Lot	46
22	Maximum Power Distribution of Lithium Cells Fabricated for the Ninth Lot	48
23	Short Circuit Current Distribution of Lithium Cells Fabricated for the Ninth Lot	49
24	Maximum Power Distribution of Lithium Cells Fabricated for the Tenth Lot	50
25	Short Circuit Current Distribution of Lithium Cells Fabricated for the Tenth Lot	51
26	Comparison of Maximum Power Distributions of Two Different Lots of Crucible Grown Lithium Cells	52
27	Comparison of Maximum Power Distributions of Crucible Grown and Float Zone Lithium Cells	53
28	Comparison of Maximum Power Distributions of Crucible Grown and Float Zone Lithium Cells	55
29	Summary of the Maximum Power Distributions of All Ten Lots	58
30	Summary of the Short Circuit Current Distributions of All Ten Lots	60

List of Tables

I	Average I_{sc} of P/N Cells	10
II	Electrical Characteristics of 20 ohm cm Float Zone P/N Cells	11
III	Average Changes in Electrical Characteristics of P/N Cells vs Sintering Time	14
IV	Lithium Cell Characteristics after Storage	24
V	Summary of all Ten Lots	56

1.0 INTRODUCTION

The goal of this contract was to investigate process parameters which might influence lithium solar cell performance. This included such areas of study as the starting material, the lithium and boron diffusions, and any other processes which were included in or might be added to the lithium cell fabrication process.

With respect to starting material, the type of crystal was of particular interest. The room temperature or low temperature recovery of lithium cells fabricated from crucible grown silicon had been a recent enough discovery that very little information had been obtained on these cells. The extremely good characteristics of these cells made them an important area for study, particularly in the early part of the contract period since their recovery after radiation is slower than the recovery of lithium cells fabricated from float zone silicon.

In general, lithium cells have had lower efficiencies than standard 10 ohm cm N/P cells. Even so, the lithium cells have compared favorably after radiation to the N/P cells. It seemed quite probable that if the efficiency could be increased, lithium cells would be an improvement over the N/P cell in a radiation environment. Since some high efficiency lithium cells were obtained in the past, the problem was one of improving uniformity and yields by improving processes and techniques. The main areas of study for improving cell efficiency were the lithium and boron diffusions and heat treatments after lithium diffusion.

A major part of this program was the fabrication of 600 experimental lithium solar cells for radiation testing and analysis by JPL. These same cells were used for statistical analyses of the short circuit current and maximum power during the contract period.

2.0 TECHNICAL DISCUSSION

2.1 PROCEDURE FOR FABRICATION OF LITHIUM DOPED SOLAR CELLS

Lithium doped P/N cells are fabricated using a procedure that has been essentially standardized. The procedures used during this program were essentially those which were being used at the beginning of the contract and any changes and improvements which were made will be described in more detail in the experimental studies section. The following description provides a brief summary of the procedures used to make lithium solar cells.

N type silicon ingots are slabbed and sliced into 0.017 inch thick blanks that are 1 x 2 cm in size. A shallow, 0.3 micron deep, P-N junction is formed by the high temperature solid state diffusion of boron into the silicon blanks using a $BC\ell_3$ source. The $BC\ell_3$ source is vaporized and carried to the silicon blanks, located in a multizoned furnace, by means of a slow constant flow of high purity nitrogen carrier gas. After boron diffusion the cells are etched on one side to expose the N base region. Finely ground lithium suspended in mineral oil is then painted on the N side and the cells are diffused and redistributed at a low temperature of about 400°C. After redistribution the cells are again back etched to clean the N surface. Ti-Ag contacts are evaporated onto the cells and a silicon monoxide antireflection coating is applied. The cells are then electrically tested by measuring I-V characteristic curves in both a tungsten light source and a solar simulator. The electrical output is highly dependent upon the type of starting material and diffusion time and temperature.

2.2 EXPERIMENTAL STUDIES

Experimental studies were performed during this contract period to determine the effect of process parameters upon lithium doped solar cell electrical and mechanical characteristics. The objective of these studies was to improve and/or develop new processing

techniques in order to obtain more economical and higher output lithium doped solar cells. Experimental procedures varied according to the parameters investigated. Some of the experiments involved detailed analysis, while others consisted of a cursory examination of a particular procedure in order to quickly evaluate the potential of a technique. Investigations of such parameters as starting material and resistivity, and lithium diffusion time and temperature were not performed as part of an experiment, rather, these parameters were evaluated by varying the design of cells fabricated for shipment to JPL. The main experimental areas studied were lithium deposition techniques, boron diffusion sources, sintering and heat treatments, etching, SiO coating, and fabrication of special cells with an N^+ region at the junction.

2.2.1 Lithium Deposition

The standard method being used for applying lithium to the cells involves careful painting of the cells with a mixture of lithium in mineral oil. Typically the size of the lithium particles varies and the layer cannot be duplicated exactly in thickness and uniformity with this paint-on technique. Since stresses generated in the silicon during lithium diffusion are dependent upon the thickness of the lithium layer and lithium particle size, painting each cell causes variations in the stresses and, quite possibly, the cell output. Application of lithium to the cell surface by evaporation would theoretically produce a far more uniform layer. The operation would be more repeatable and would virtually eliminate problems of particle size. Variations in the thickness of the lithium layer would be minimal and, therefore, the stresses produced in the silicon during lithium diffusion would be reduced. Evaporation of lithium onto a quantity of cells would also be far less tedious than painting each individual cell.

Initial investigations of lithium evaporation showed that the cell V/I measurements were less uniform than with the standard painted source. The cells had more series resistance and lithium oxidized during transferral from the vacuum to the diffusion furnace. Since the oxidation of lithium during transferral from the vacuum system to the diffusion furnace was suspected to be the cause of the other two problems, methods of reducing or eliminating this oxidation were investigated. These methods involved evaporation of some other material to cover the lithium in order to protect it from air and moisture. Three different materials have been investigated during the past year, namely Aℓ, Ag, and SiO.

Aluminum was the first material investigated. Rapid oxidation occurred spontaneously and instantaneously when air was let into the vacuum system and the Li-Aℓ layer peeled and flaked off the cells. By leaking the air in more slowly some evaporations were obtained in which the Li-Aℓ layer did not peel and flake off. The cells were diffused 90 minutes at 425°C. After diffusion V/I's were measured using the four point resistivity probe and they varied more than V/I's measured on cells where lithium was painted on. For the particular diffusion parameters used the V/I's normally vary from .22 to .28, but when the aluminum protective evaporation was used V/I's ranged from .22 to 1.21. Since the V/I range was large and it was difficult to remove the cells from the vacuum system without rapid oxidation occurring, aluminum was eliminated as a suitable coating material.

Another protective coating material investigated was silver. An evaporation was set up such that cells which had a thicker layer of lithium had a thinner layer of silver and vice versa. The result was peeling on the cells with the thicker lithium and thinner silver layers, indicating a porous silver layer. The amount of lithium was subsequently decreased and silver increased. The resulting layers did not peel so these cells were diffused. V/I's were measured,

but they indicated that no significant lithium diffusion occurred. This could have been caused by one of two things. Either the lithium partially oxidized before the cells were put into the diffusion furnace or the lithium did not alloy to the cell surface and therefore did not diffuse. The Li-Ag layer reacted when a couple of cells were dropped into water after the evaporation, so the lithium metal was present for diffusion. Therefore, it appears that for some reason the lithium did not alloy. Further investigation showed that the lithium was preferentially alloying to the silver layer instead of the silicon. Consequently the lithium was not reproducibly alloying and diffusing into the silicon, making this technique an unsatisfactory one.

Investigations of SiO cover layers on top of the lithium have also been performed. After diffusion with this system a smooth brown layer was present which subsequently peeled off. Hot point probing and four point V/I measurements indicated that either no significant lithium diffusion had occurred or some type of insulating barrier was present. This may have been due to a chemical reaction or a deposited layer from incomplete removal of SiO. Chemically etching the cells in HF resulted in no change in the hot point probe and V/I measurements. Measurements made after lapping approximately 0.005 inches off the lithium diffused surface, however, indicated that lithium had diffused into the cell. Use of an $HF\text{-}HNO_3$ acid etch also removed the insulating barrier and made it possible to measure V/I's. These measurements indicated that a lower than normal lithium concentration had been obtained. Use of the paint-on technique for a 90 minute diffusion at 425°C typically results in a lithium surface concentration of $\approx 10^{17}$ atoms/cc; whereas, with the evaporation technique and the same diffusion parameters, V/I's indicate a lithium surface concentration of $\approx 10^{16}$ atoms/cc. The work with the Li-SiO layer was done on silicon blanks thus far, and due to lack of time the technique has not been used on cells. The process

should be further evaluated with respect to cell output, V/I's, uniformity of these measurements and repeatability. The advantages of applying lithium by evaporation are important in considering large scale production of lithium cells. Therefore, this SiO protective layer technique should be further investigated.

2.2.2 Lithium Diffusion

Variations in the electrical characteristics of lithium cells have been one of the biggest problems. In general, these variations were present in every lithium diffusion lot. For this reason several lithium diffusion variables were investigated with respect to influence, if any, upon cell output. The elimination of severe pitting sharply reduced cell breakage, but this did not reduce the variations in electrical characteristics. Other lithium diffusion variables studied were cleanliness of the parts and cell position on the boat during diffusion. With respect to cell position during lithium diffusion, it was postulated that the oil vapors coming off the cells first exposed to the carrier gas could contaminate the cells in the next row or the lithium source could be depleted on cells in the first row and increased on cells in the second row. Either of these situations might cause cells in one row to have different I-V characteristics than the cells in the other row. In an attempt to see such an effect, several lithium diffusions were separated according to rows and processed with identity maintained. When I-V curves were analyzed it was found that no correlation between output and cell position on the diffusion boat could be made. In each row there were cells with both high and low short circuit currents.

During lithium diffusion the mineral oil in which the lithium is suspended vaporizes. Much of it is carried out of the quartz tube by the carrier gas flow; however, some of it condenses on the cold end of the tube and after several diffusions the tube end has a heavy buildup. The cells are inserted into the furnace at this

same end of the tube and it was postulated that the boat could carry in a contaminant. To check this, three diffusions were made, where after each diffusion and redistribution the tube was changed. The average short circuit current measured in a tungsten light source for this group of cells was 39 mA with a range from 35 to 43 mA. Typically the short circuit current is about 5 mA higher. The use of two dummy runs prior to a standard lithium diffusion resulted in cells with short circuit currents ranging from 40 to 50 mA. This verified that the collection of oil on the diffusion tube did not affect the diffusion and that a break-in period for clean tubes was beneficial.

Another area investigated for improvement of cell output and/or processing techniques was the effect of back etching. Up to this time back etching was done twice during the fabrication process: first after the boron diffusion to remove the P layer, and then after lithium diffusion and redistribution to remove a portion of the lithium diffused surface and clean the back surface. The primary reason for this investigation was that the double etching could be harmful and/or unnecessary. Exactly the same edge area would not be etched the second time and it was postulated that areas previously etched could thus become contaminated. This could result in a poorer I-V characteristic curve. Use of only one back etch could, therefore, improve the cell characteristics. Tests showed that lithium could be satisfactorily diffused through the boron layer. Therefore, the back etch prior to lithium diffusion was the etch step selected for elimination. Cells which were not back etched prior to lithium diffusion were compared to cells which were etched (see Figure 1). Average outputs for cells from ten lithium diffusions done during the same time period and using the same material and diffusion parameters are shown. Three groups of cells were not etched prior to diffusion, the other seven were. There was no definite indication that etching prior to lithium diffusion resulted in improved output. In fact, the

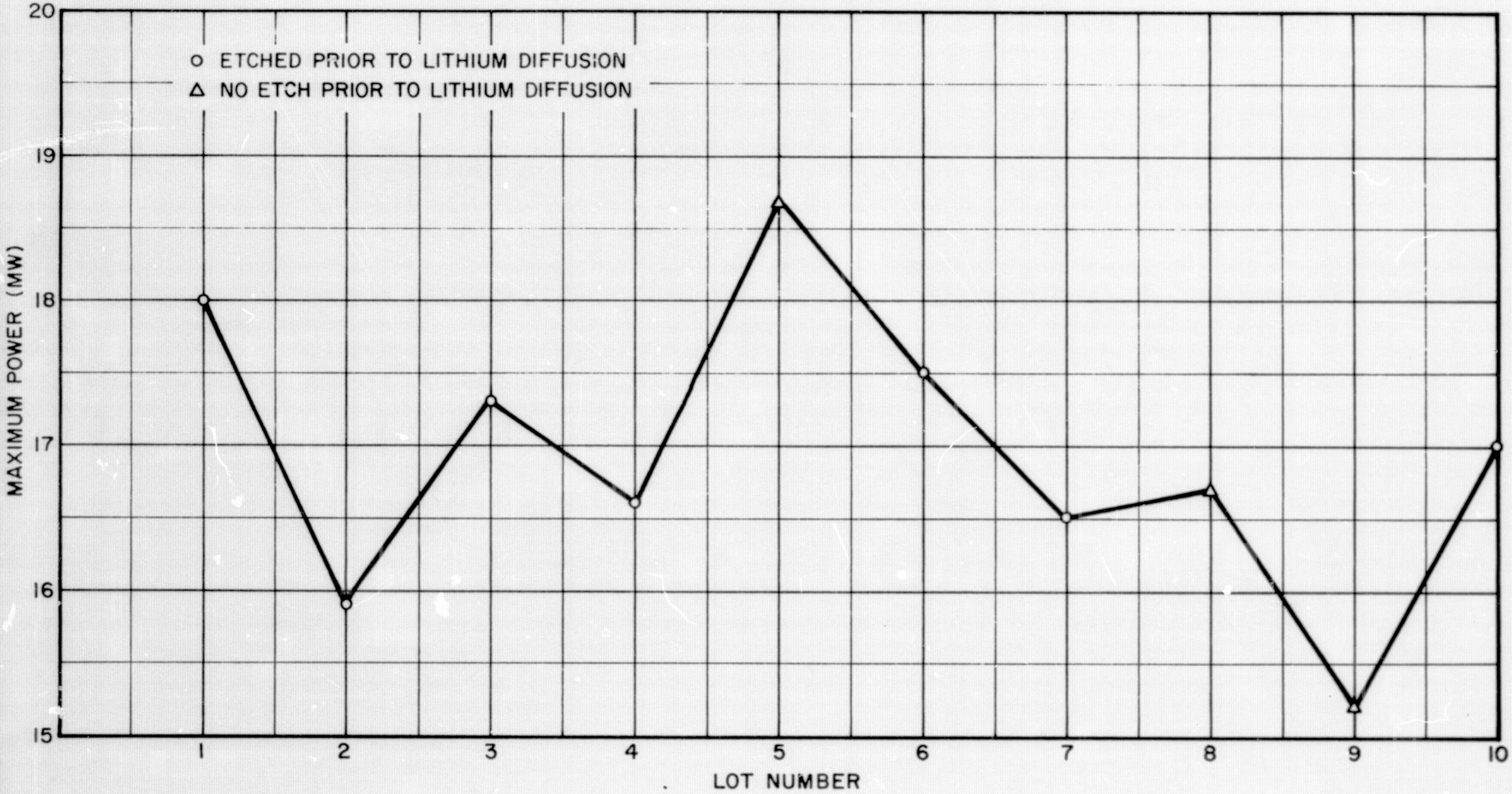


Figure 1. Average Cell Outputs from Ten Lithium Diffusions. Measured in Tungsten.

highest and lowest output groups were obtained with the non-etched process. Since omitting the etching showed no significant decrease in output and gave the advantage of fewer processing steps and less handling, the etching prior to lithium diffusion was eliminated.

2.2.3 Antireflection Coating

The object of this study was to determine whether the dark blue layer obtained naturally in boron diffusion resulted in higher or lower output than that obtained with SiO used as an antireflection layer. In the standard fabrication procedure, the blue layer obtained during boron diffusion was removed by an HF acid etch before contact application, leaving a grey to grey-blue surface which is later covered with a SiO antireflection coating. In this experiment the short circuit currents of cells with a standard SiO antireflection coating were compared to the short circuit currents of cells which did not have the blue layer from boron diffusion etched off. I-V curves of both groups were measured in a 100 mW/cm^2 tungsten light source and in the Spectrosun solar simulator at an intensity of 140 mW/cm^2. Table I shows the average short circuit current values obtained from the two groups of cells; Group A had the SiO coating and Group B had the blue layer from boron diffusion. Before SiO coating, the average I_{sc} of the cells in Group A was lower than the average I_{sc} of the cells in Group B - 53.0 versus 55.0. However, when Group A cells were SiO coated, the average I_{sc} in a 100 mW/cm^2 tungsten light source was 59.8 mA, which was approximately 9% higher than the I_{sc} of Group B cells. When Group A and B cells were measured in the solar simulator, the difference between the two groups' average I_{sc} decreased to about 6.5%; however, on an absolute scale, the difference between the short circuit currents of Groups A and B measured in the simulator and in tungsten was nearly the same -- 5.8 mA difference in the simulator versus 4.8 mA in tungsten. After measuring the I_{sc} of Group B cells in the simulator and

finding it to be lower than the I_{sc} of Group A cells, a SiO layer was evaporated over the blue layer of Group B cells. This only increased the average I_{sc} 1.3 mA, indicating that the blue layer-SiO layer is optically inferior to the antireflective layer obtained by SiO coating a cell without the blue layer.

TABLE I

Average I_{sc} of P/N Cells

SiO Layer versus Blue Layer from Boron Diffusion

Light Source	Type and/or Condition of Antireflection Layer	I_{sc}, mA
Group A (8 cells)		
100 mW/cm^2 tungsten	before SiO coating	53.0
100 mW/cm^2 tungsten	after SiO coating	59.8
140 mW/cm^2 solar simulator	after SiO coating	71.8
Group B (8 cells)		
100 mW/cm^2 tungsten	blue layer from boron dif.	55.0
140 mW/cm^2 solar simulator	blue layer from boron dif.	66.0
140 mW/cm^2 solar simulator	blue layer and SiO	67.3

2.2.4 Boron Diffusion

The boron diffusion was also studied in order to improve the uniformity and output of lithium doped solar cells. Experiments were performed to study the etch pattern caused by the BCl_3 diffusion source and its effect upon cell output. Evaluation of P/N cells without lithium showed that cell position during boron diffusion affected the electrical output. During boron diffusion silicon is etched away from the slices by the chemical reaction of the BCl_3 gas. The amount of etching varies, but those silicon slices which

are first exposed to the gas flow are etched more than the cells "down stream" on the diffusion boat. The cells which are etched more have lower outputs than those with less etching. Table II shows the I_{sc} and I at 400 mV of 20 ohm cm float zone cells diffused in the same boron diffusion. The measurements were made in a 100 mW/cm^2 tungsten light source. The data shows the very definite difference in I_{sc} depending upon cell position during boron diffusion.

TABLE II

Electrical Characteristics of 20 ohm cm F.Z. P/N Cells

Cell Position on Diffusion Boat	I_{sc}, mA	I@ 400 mV mA
Back	61.7	56.0
"	61.5	55.7
"	61.0	55.2
"	60.4	54.4
Front	58.2	51.8
"	57.0	50.5
"	53.5	47.0
"	58.0	51.5

The average I_{sc} of the cells at the front of the boat was 56.7 mA and this average increased to 61.1 mA for the cells at the back of the boat. One method investigated to eliminate these variations in output involved trying to change the boron flow pattern by placing flow deflector in front of the boat of cells. The cells were not sifnificantly affected; therefore, either the flow pattern was not altered sufficiently or the alteration did not effect a simultaneous change in the etch pattern. Diffusing fewer cells at a time resulted in more uniform output; however, the output was lower than normal. This can be explained by the fact that the etching on these cells resembled that which occurs on the front

cells (which have the lower output) of a standard size diffusion. Diffusing fewer cells and using some dummy cells at the front of the boat resulted in high cell output as well as good uniformity. This technique was consequently used for the majority of the cells fabricated during this contract.

Use of $BC\ell_3$ diffusion source results in high output cells; however, the number of cells per diffusion is limited and due to the etching action of the $BC\ell_3$, it is not the optimum source for special cell types.

For these reasons other boron diffusion sources have been investigated. The emphasis has been placed on finding a suitable diffusion for the special cell with an N^+ surface which had to be overcompensated. Thus far, BN, Borofilm and B_2H_6 have been investigated. The BN source did not overcompensate the N^+ surface and form a good junction and since it offered no advantages in cell output and handling, it was not pursued. Study of Borofilm as a paint-on source was limited to investigation of its ability to overcompensate the N^+ surface. Overcompensation occurred only when a very thick layer of Borofilm was applied, and then a brown residue which could not be removed was left on the cell surface. Since the procedure did not work well for the special cell and offered less advantages than a good gas system, no further investigation of Borofilm was done. A diffusion furnace has been set up with diborane, B_2H_6, as a source, but at this point the diffusion process has not yet been worked out. So far the cells diffused in diborane have had low short circuit currents. Extensive work will be done on this diffusion since, when perfected, it will offer many advantages. It does not etch silicon during diffusion and therefore, would be valuable for the special cell with the N^+ region. Also, it does not stress the cells as $BC\ell_3$ does. This was shown by the lack of any bowing of large area dummy cells which have been placed in the diffusions. In addition, the number

of cells/diffusion would not be limited as with BCl_3 diffusions.

2.2.5 Sintering

For standard lithium cell processing, sintering Ti-Ag contacts has not been utilized since good ohmic contact is obtained without sintering. From time to time the series resistance of some cells was higher than normal. This along with some initial work suggested that higher efficiencies might be obtained by sintering P/N cell contacts. For these reasons a study of the effects of sintering P/N cells with and without lithium was started during this contract.

Evaluation of the effect of sintering on lithium cells involves investigation and analysis of two aspects: the effect of sintering Ti-Ag contacts on P/N cells and the effect of high temperature heat treatment of lithium diffused cells. These two things cannot be completely separated in evaluating lithium cells; however, by also studying P/N cells without lithium, just the effect of sintering Ti-Ag contacts on P/N cells could be evaluated. Information from comparative studies such as this has been useful in evaluating the effects of sintering lithium doped cells.

In one such experiment a group of thirty-seven 20 ohm cm P/N cells without lithium were divided into three sub-groups: the first was sintered three minutes, the second six minutes, and the third twelve minutes at 600°C. In each of these groups similar changes occurred; however, in most cases the degree of change varied with the sintering time. Losses occurred in maximum power, open circuit voltage, and curve factor, whereas, increases occurred in the short circuit current. The average increases and decreases in these values are shown in Table III.

TABLE III

Average Changes in Electrical Characteristics
of P/N Cells vs Sintering Time

Sintering Time, min.	ΔI_{sc} mA	ΔV_{oc} mV	ΔP_{max} mW	ΔC.F.
3	+4.0	- 23	- .1	- .015
6	+3.3	- 38	- 2.1	- .022
12	+3.8	- 44	- 3.0	- .042

The increases in the short circuit current did not seem to be highly dependent upon the sintering time. In the cases of V_{oc}, P_{max}, and C.F. the sintering time did have an effect: with increasing sintering time, greater losses occurred. The primary cause of the decreases in P_{max} and C.F. was the significant loss in voltage in all the cells. Without the voltage loss the increase in short circuit current would have resulted in an increase in the maximum power, since the series resistance and curve factor were not significantly affected. The voltage loss is indicative of the formation of some type of barrier. In associated experimental work being done to develop an aluminum contact on P/N lithium cells, one experiment involved subjecting P/N cells without lithium having Aℓ grid lines and Ti-Ag back contacts to multiple sinterings in order to study the effect upon the metal contacts. These cells were sintered once with the Aℓgrid lines only, and then two more times after application of the Ti-Ag back contacts. There were increases in maximum power, open circuit voltage, and short circuit for these cells which would indicate the two sintering processes did not adversely affect the Ti-Ag back contact even with two sintering steps. Applying this information to the current studies on cells with Ti-Ag front and back contacts would indicate that the barrier being formed is at the front contact although experience has indicated that the barrier is usually on the back.

The work on lithium cells included investigating effects of 600°C multiple sinterings and the effect of sintering on low short circuit current output (possibly stressed) lithium cells. I-V curves were taken of a group of cells before and after three sinterings. The results obtained from a typical cell are shown in Figure 2. After the first sintering a significant increase in short circuit current (6%) was observed and, due to increased series resistance, an extreme decrease in curve factor (16%) occurred. After a second sintering the short circuit current again increased (an additional 2%) and the curve factor improved, although it was still lower than the original value. At this point the maximum power, which had initially been 24.3 mW and had subsequently dropped to 21.5 mW after the first sintering, had increased to 24.7 mW. A third sintering resulted in another slight increase in short circuit current; however, the series resistance again increased. The results of this experiment show that the short circuit current increased with each sintering step. The initial increase of 3.6 mA was approximately twice that of each successive increase and was probably due not only to lithium movement (possibly outgassing and/or migration to the boron diffused layer), but also to a gettering action. The latter seems to be supported by the fact that short circuit current increases also occur when P/N cells without lithium are sintered. Another factor which could be involved in the changes which occur with sintering is stress relief. Some of the sintering work has shown such substantial increases in the short circuit current of some cells (especially very low I_{sc} cells) that it seems unlikely that it can be accounted for by the same type of mechanism which occurred in the cell shown in Figure 2. Figures 3 and 4 show a group of cells before and after sintering which explains this effect in more detail. In Figure 3 there are two very distinct groupings of I-V curves for cells processed to the same stage by the same techniques. One group has short circuit currents ranging

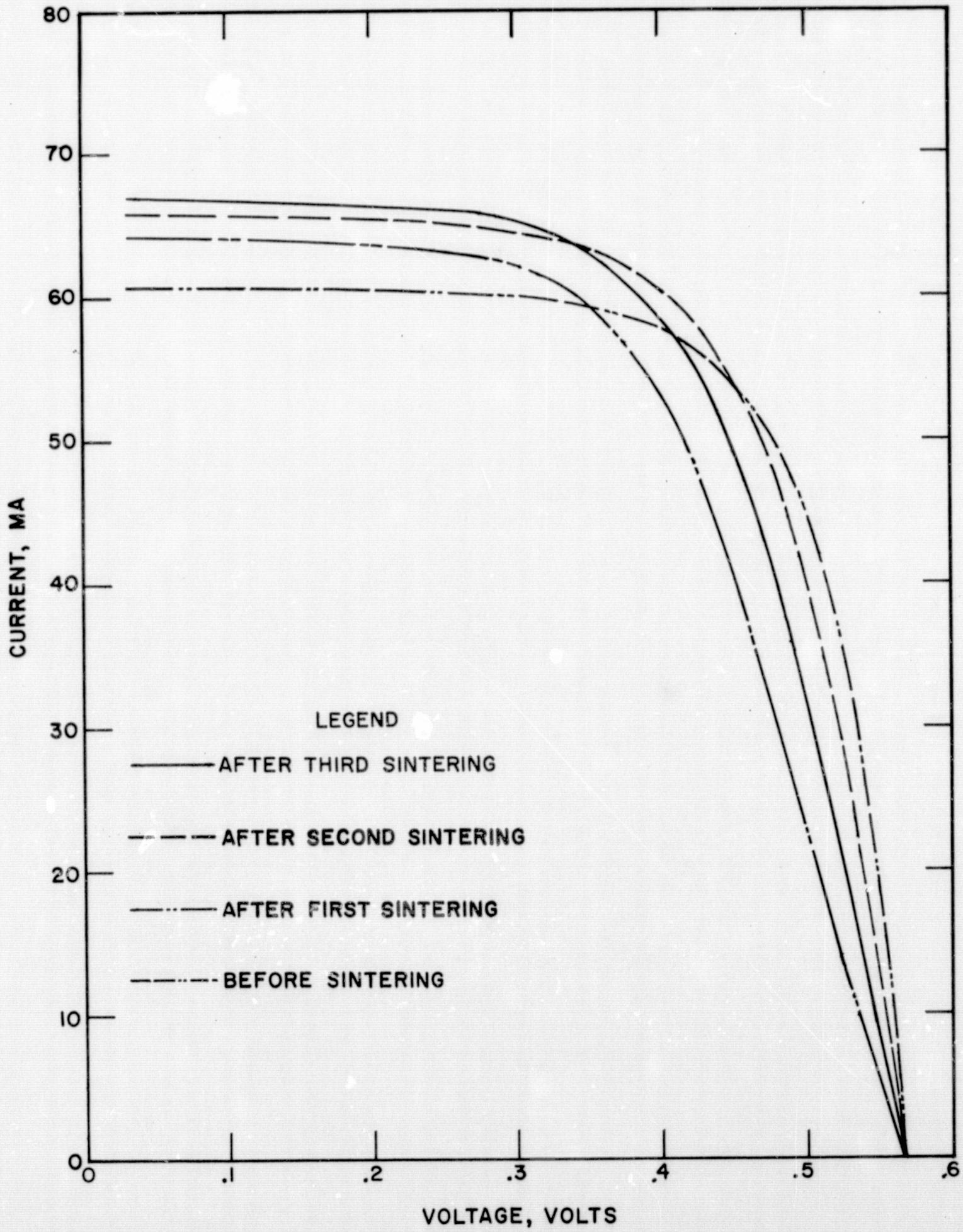


Figure 2. I-V curves Before and After Sintering Lithium Diffused P/N Cells. Measured in Solar Simulator at 140 mW/cm2; 28°C Cell Temperature.

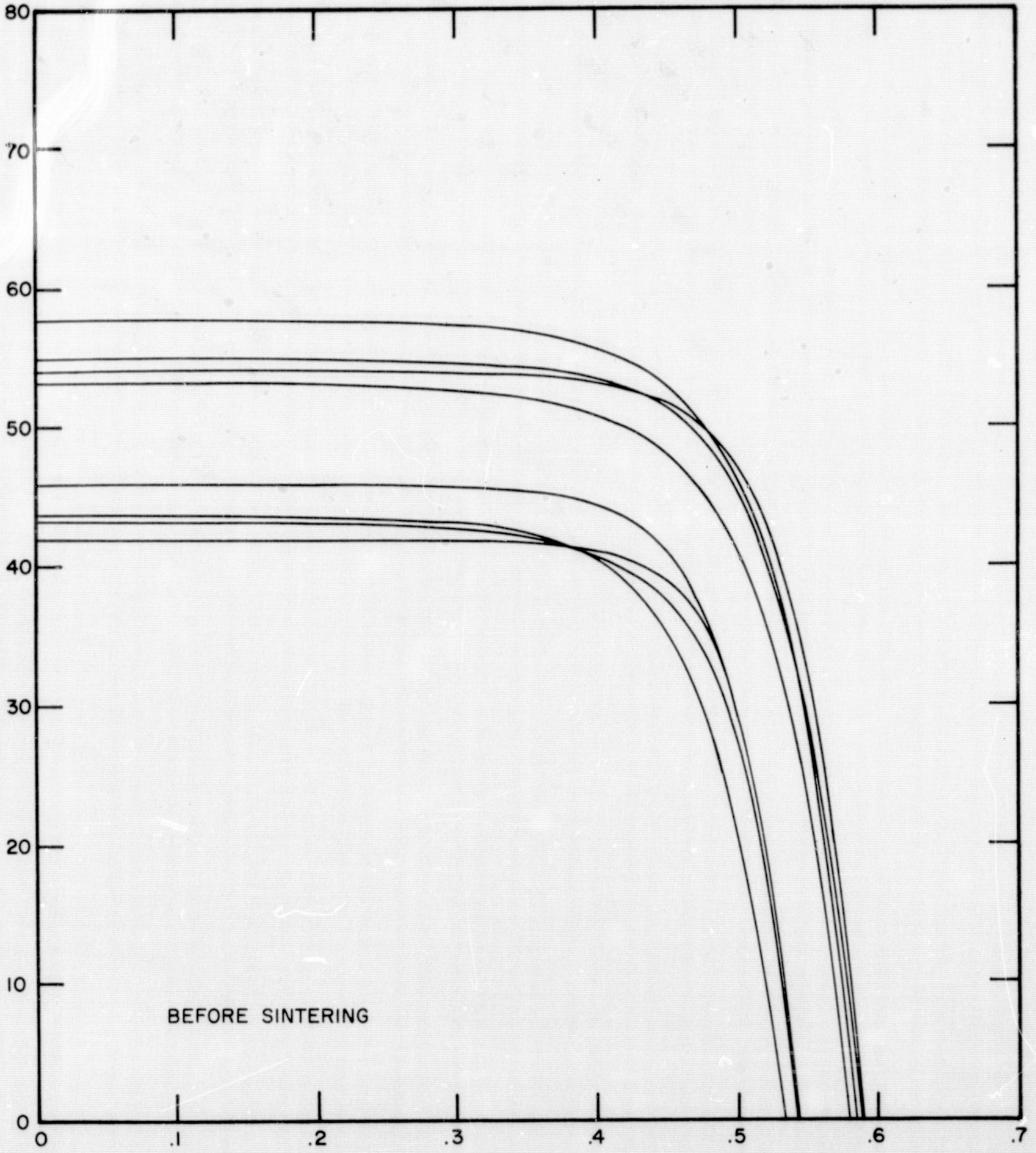


Figure 3. I-V Curves of an Unsintered Lot of Lithium Diffused P/N Cells. Measured at 28°C in 100 mW/cm^2 Tungsten Light Source.

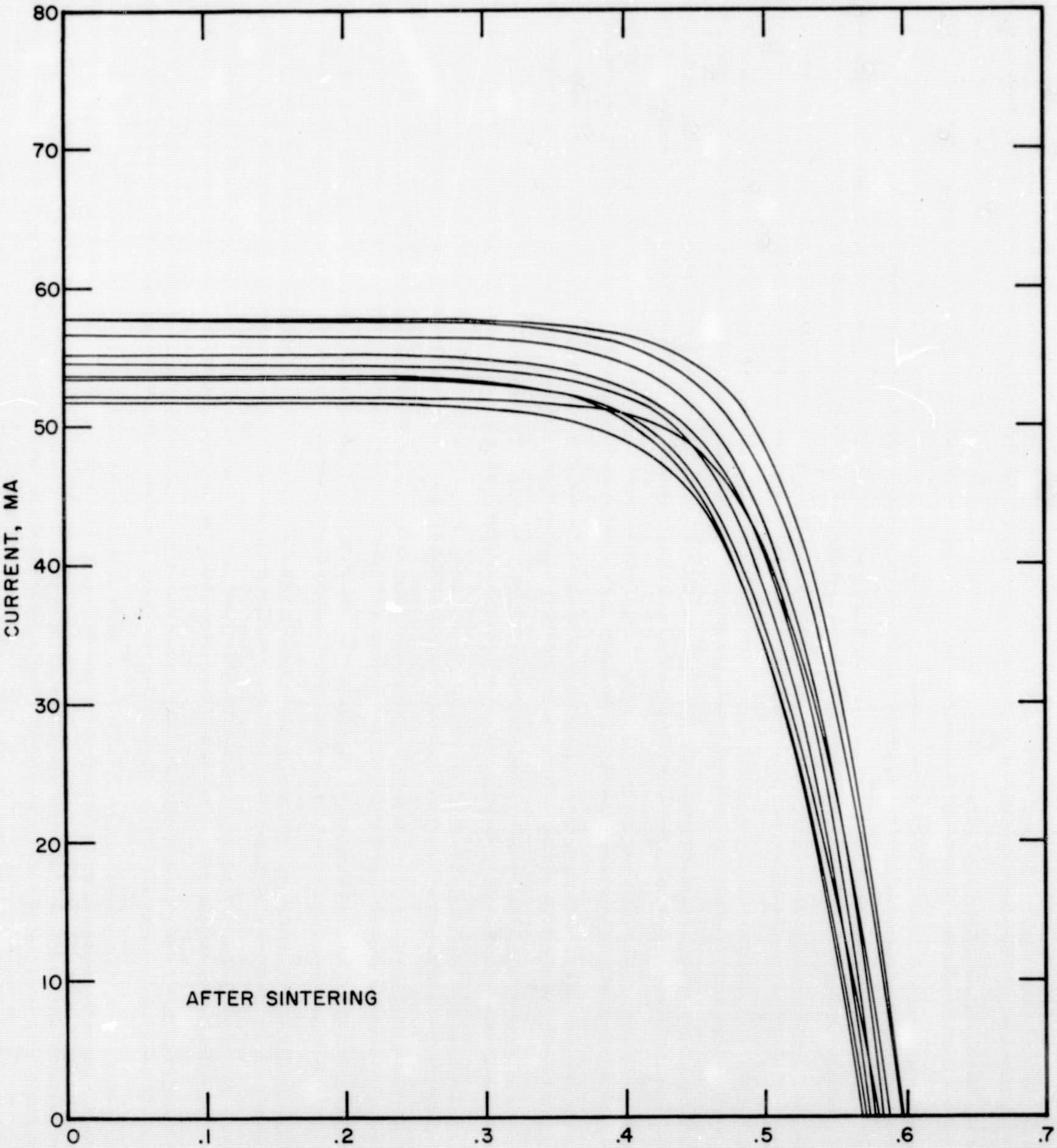


Figure 4. I-V Curves after Sintering of the Lot of Lithium Diffused P/N Cells shown in Figure 3. Measured at 28°C in 100 mW/cm^2 Tungsten Light Source.

from 42 to 46 mA; the other group ranges from 53 to 58 mA. The maximum power values and open circuit voltages are similarly grouped. These two groupings were obtained on cells which lithium diffused in the same diffusion run; however they came from two different boron diffusion runs. The significance of this will be discussed later; the point to be made is that the difference in I-V characteristics cannot be correlated to the lithium diffusion. Sintering these cells resulted in the significant changes shown in Figure 4. As expected, the short circuit current (as well as the open circuit voltage and maximum power) of the cells increased; however, the low output cells showed much greater increases than the high output cells. The average short circuit current of the low cells increased 22% after sintering while the high output cells increased only 2%. The total group of cells had a short circuit current range of 52 to 58 mA after sintering which was a considerable improvement over the 42 to 58 mA range prior to sintering.

This same effect of greater improvements in low output (possibly stressed) cells than in higher output cells, was observed when cells fabricated for the tenth lot shipment were sintered. In a group of 43 cells fabricated, 35 had AMO outputs greater than 28.0 mW with the average output being 30.5 mW. The other 8 cells had outputs ranging from 25.3 to 27.9 mW. Four of these lower output cells and one with an output of 29.0 mW were sintered to evaluate the respective improvements available. Figure 5 shows the I-V curves of a typical low output cell measured in a tungsten light source before and after sintering. The short circuit current increased 20%, the open circuit voltage 4.5% and the maximum power 25%. In the simulator these parameter changes corresponded to 15% for short circuit current, 18% for maximum power and 3% for open circuit voltage. Figure 6 shows the improvement made by the initially higher output cell. This increase in output was substantial, but not as high as that obtained with the low output cell. The short current increased 12%, the open circuit voltage,

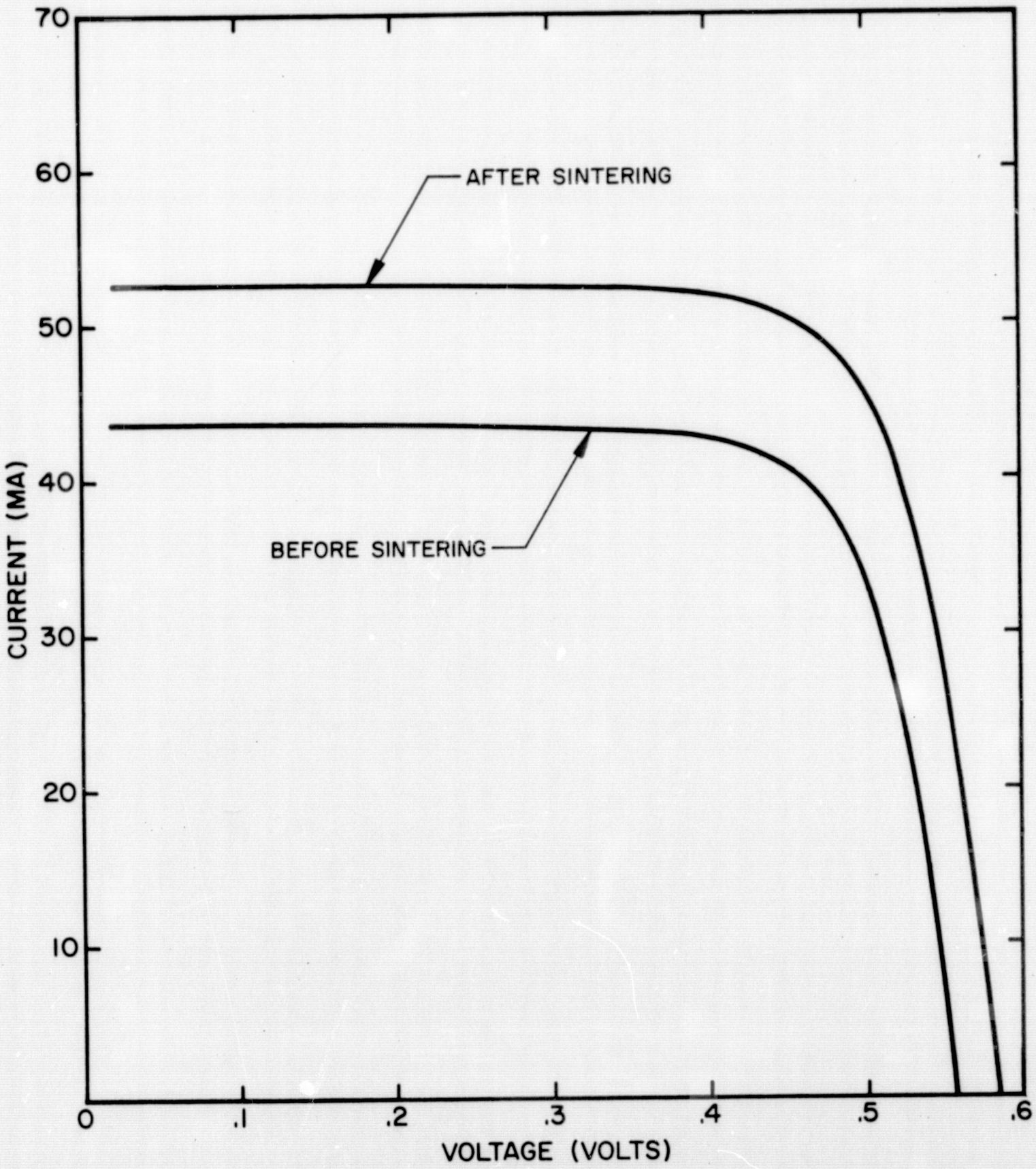


Figure 5. I-V Curves Before and After Sintering of a Low Output Lithium Diffused P/N Cell. 20 ohm cm Czochralski Grown cell measured at 28°C in 100 mW/cm^2 Tungsten Light Source.

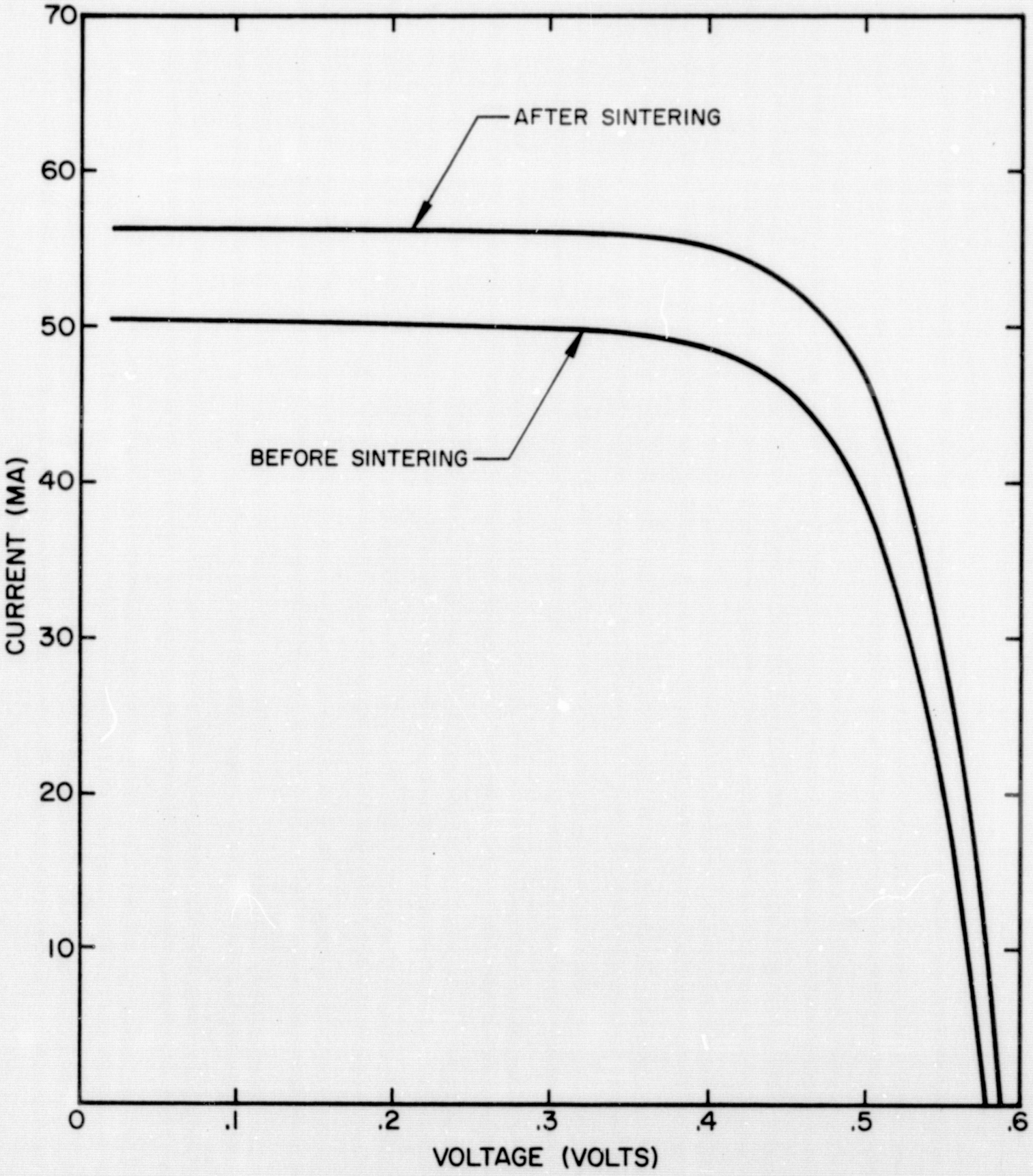


Figure 6. I-V Curves Before and After Sintering of an Average Output Lithium Diffused P/N Cell. 20 ohm cm Czochralski Grown cell measured at 28°C in 100 mW/cm^2 Tungsten Light Source.

1.4% and the maximum power, 10.6%.

The following ideas are possible explanations of the various degrees of improvement resulting from sintering lithium cells. The stresses in the silicon caused by the boron diffusions can vary from one diffusion run to another. This has been obvious since some diffusion runs have actually bowed cells while most do not. These variations in the stresses in the cells probably cause the lithium to enter the silicon lattice in a different energy state, such that the electrical characteristics would be affected. The sintering then produces an annealing action where the stresses are relieved and/or re-arrangement of the atoms occurs which causes improvements in the electrical characteristics. Or, the problem may originate in the lithium diffusion and be related to the stresses caused by particle size, amount of lithium, and/or variations in the alloying process. At any rate, these changes resulting from sintering indicate that both cell output and uniformity are strongly related to heat treatments or sintering processes used to make lithium cells. Investigation must still be done to determine whether or not this will be the case for all types of lithium cells and what conditions are the optimum ones for high output cells. In addition feedback information on the effects of this type heat treatment on radiation resistance will be an important consideration.

2.2.6 STORAGE LIFE

Since lithium moves about in the silicon crystal lattice at room temperature, lithium doped solar cell electrical characteristics might be expected to change with storage at room temperature. In order to monitor any such changes, cells which were fabricated 2-1/2 years ago under NASA Contract NAS5-10272 have been measured periodically. The cells being monitored were fabricated and initial measurements were made between September and November 1966. At that time the quantity of lithium cells being fabricated was much smaller than current levels and many different diffusion times, redistribution times, and diffusion temperatures were being investigated. Since a number of these cells were single cell samples for a particular set of diffusion parameters or had diffusion parameters which are of no particular interest at the present time, i.e., 5 minute diffusions and 500°C diffusions, they were not included in this discussion although they are still being monitored.

Table IV shows the I_{sc}, V_{oc}, and P_{max} obtained initially around October 1966; those obtained 14 months later in January 1968, and those obtained after approximately 2-1/2 years in March 1969. From October 1966 to January 1968, there was very little change in the 1 ohm cm and >100 ohm cm crucible grown cells diffused at 425°C. By March 1969 increases of 1.0-2.0 mA in short circuit current, and .5-1.0 mW in maximum power had occurred. The open circuit voltages improved about 5 mV except in two cases: one cell stayed the same, the other lost 6 mV. The 20 ohm cm float zone cells diffused at 425°C showed increases mostly in short circuit current in two out of three cells. The third cell (#101) showed approximately 3 mA loss in short circuit current, 36 mV loss in open circuit voltage and approximately 3 mW loss in maximum power. The 100 ohm cm float zone cells diffused at 425°C also had varied results. One cell showed slight increases in the short circuit current, while the open circuit voltage and the maximum power stayed about the same.

Cell No.	Material	Diffusion Condition	I_{sc} 1	I_{sc} 2	I_{sc} 3	V_{oc} 1	V_{oc} 2	V_{oc} 3	P_{max} 1	P_{max} 2	P_{max} 3
48	1 ohm cm CG	90/60 425°C	61.5	61.9	63.1	600	600	605	28.6	28.5	29.0
66	1 ohm cm CG	90/60 425°C	62.0	62.5	64.0	594	600	600	27.1	27.6	28.1
71	1 ohm cm CG	100/60 425°C	63.8	63.3	64.8	603	605	608	29.4	29.2	30.0
82	>100 ohm cm CG	90/60 425°C	54.6	54.9	57.0	556	550	550	21.5	21.4	22.0
83	>100 ohm cm CG	90/60 425°C	53.2	53.8	55.9	541	540	540	19.6	19.7	20.4
93	>100 ohm cm CG	90/60 425°C	57.4	57.8	59.0	576	578	580	22.3	22.3	23.0
101	20 ohm cm FZ	90/60 425°C	55.4	51.0	52.6	559	532	523	23.4	20.3	20.7
155	20 ohm cm FZ	90/60 425°C	58.0	58.0	59.8	555	550	554	23.2	23.2	23.9
156	20 ohm cm FZ	90/60 425°C	56.5	56.9	58.8	547	542	549	22.7	22.8	24.0
85	100 ohm cm FZ	90/60 425°C	57.5	53.0	55.0	562	543	538	24.1	21.6	22.0
86	100 ohm cm FZ	90/60 425°C	55.2	51.0	53.4	553	530	525	22.9	20.4	21.0
158	100 ohm cm FZ	90/60 425°C	59.0	57.9	59.3	563	556	560	24.0	21.2	24.0
112	20 ohm cm FZ	90/60 350°C	68.8	67.5	68.3	560	549	552	28.0	27.3	27.7
136	20 ohm cm FZ	90/60 350°C	64.5	65.0	66.7	582	573	572	27.9	27.9	28.6
130	100 ohm cm FZ	90/60 350°C	65.2	63.5	64.0	581	568	569	27.1	26.2	27.0
131	100 ohm cm FZ	90/60 350°C	64.3	63.0	64.0	572	560	560	26.9	26.0	26.5
139	100 ohm cm FZ	90/60 350°C	65.4	64.4	65.5	585	573	575	28.0	26.2	27.7

(1) Initial measurements made ≈ October 1966

(2) Measurements made January 1968

(3) Measurements made March 1969

The other two cells showed decreases in all three characteristics, with the open circuit voltage and maximum power losses being particularly significant. The 20 and 100 ohm cm float zone cells which were diffused at 350°C showed slight losses in output after 14 months; however, the most recent measurements showed some improvement and the outputs of these cells after 2-1/2 years are less than 0.5 mW lower than the initial outputs.

The float zone cells lithium diffused at 425°C in some cases showed slight improvements and in others showed significant losses. In all the cells which had significant losses there were large decreases in the open circuit voltage, whereas, in all the other cells there was little change in the open circuit voltage.

Cells which were made early in this year's contract were also remeasured in order to check for short term changes. The Mon-x and float zone cells fabricated for Lots 3 and 4 showed significant short circuit current losses -- 2.5-4.0 mA. The crucible grown lithium cells did not change.

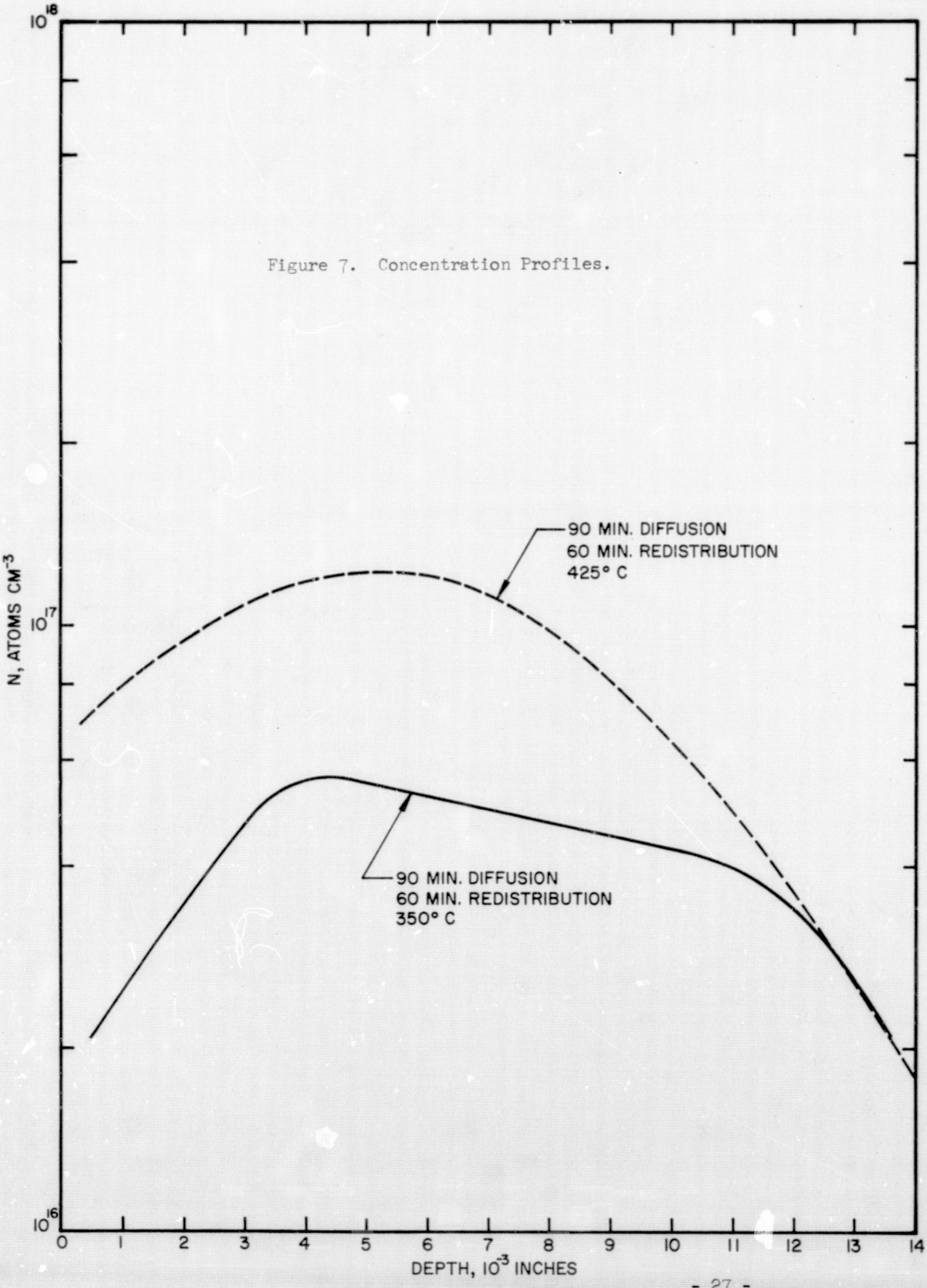
2.3 CELLS DELIVERED TO JPL

Ten lots of sixty lithium doped cells each were shipped to JPL during the contract. In fabricating the required sixty cells for each lot, usually more cells were diffused, processed and tested. This resulted in groups large enough for good selection and also provided a large number of cells for statistical analysis. This statistical analysis was made using all cells produced, rather than just the sixty cells selected for shipment to JPL in order tc avoid biasing the analysis.

In fabricating the cells for the ten shipment lots, the lithium diffusion time of 90 minutes and redistribution time of 60 minutes were kept constant. Eight out of the ten lots were lithium diffused at 425°C; the other two lots were diffused at 350°C and 450°C. For reference purposes, Figure 7 shows typical lithium concentration profiles for 90 minute diffusions with 60 minute redistributions at 350°C and 425°C. The lithium distributions in most of the cells shipped to JPL, therefore, would resemble the higher concentration curve characteristic of the 425°C diffusion. The back half of the cell would have a lithium concentration around 10^{17} atoms/cm^3 with the concentration dropping to less than 10^{16} atoms/cm^3 at the junction. Diffusing at 350°C results in a lithium concentration approximately half that obtained at 425°C. No lithium concentration curve was determined for diffusion at 450°C; however, the lithium concentration would not be much higher than that obtained at 425°C since much outgassing would occur during redistribution at this temperature.

Due to the time required to obtain radiation recovery data on crucible grown lithium cells, these cells were selected by JPL for fabrication for the first shipment. Lot 1 consisted of > 100 ohm cm crucible grown silicon, lithium diffused 90 minutes and redistributed 60 minutes at 425°C. As shown in Figure 8, 50% of the cells had a maximum power greater than 26.0 mW, 95% of the cells were above

Figure 7. Concentration Profiles.



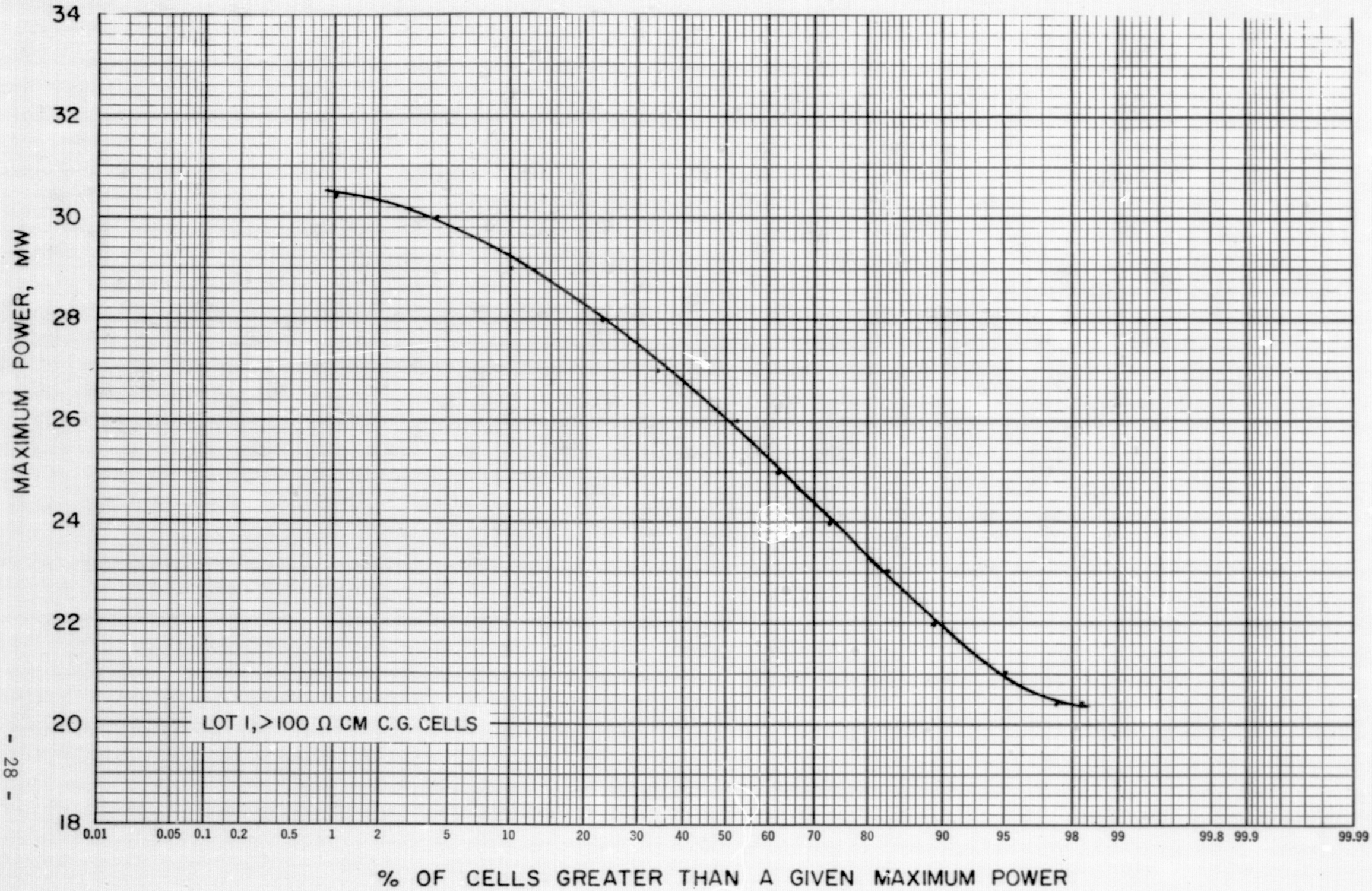


Figure 8 Maximum Power Distribution of Lithium Cells Fabricated for the First Shipment Lot. >100 ohm cm Czochralski Grown silicon, diffused 90 minutes, redistributed 60 minutes at 425°C. 120 cells measured in solar simulator at 140 mW/cm^2.

22.0 mW and 5% were above 21.0 mW. Figure 9 shows the short circuit current distribution for this same lot of cells. The spread in short circuit current was rather wide with 5% of the cells above 68.2 mA, 50% above 62 mA, and 95% above 54.2 mA.

The second lot was fabricated from 20 ohm cm crucible grown silicon and had the same diffusion parameters as Lot 1. Figure 10 shows two maximum power distributions of cells fabricated for the second shipment lot. The lower curve includes all the cells fabricated while the upper curve has five diffusion runs eliminated. These five diffusion runs were consecutive and the average cell output for all five runs was conspicuously lower than the cells from runs before and after. The cause of the lower output cells was not determined; however, the fact that the diffusion runs were consecutive and highly unusual would seem to indicate that some diffusion variable went out of control for one to two days. Both distributions show an improvement over the first shipment distribution. Even considering the lower curve the maximum power 50% point increased from 26.0 mW for the first lot to 27.9 mW for the second lot. In the second lot 95% of the cells were above 22.9 mW and with the five runs eliminated 95% were above 26.0 mW. Figure 11 shows short circuit current distributions with and without the five diffusion runs eliminated. The short circuit current 50% point of the lower distribution was 63.7 mA, 5% of the cells were higher than 69.4 mA and 95% were above 56 mA. The corresponding values for the higher distribution were 66.3 mA, 69.5 mA, and 60.3 mA.

The only differences between lots 1 and 2, besides the time period of fabrication, were the resistivity of the starting material and the boron diffusions. The boron diffusions for the second lot used dummy cells in an attempt to reduce the etch rate and electrical output variations. Both lots were doped to the same level with lithium. It is unlikely that the starting material resistivity

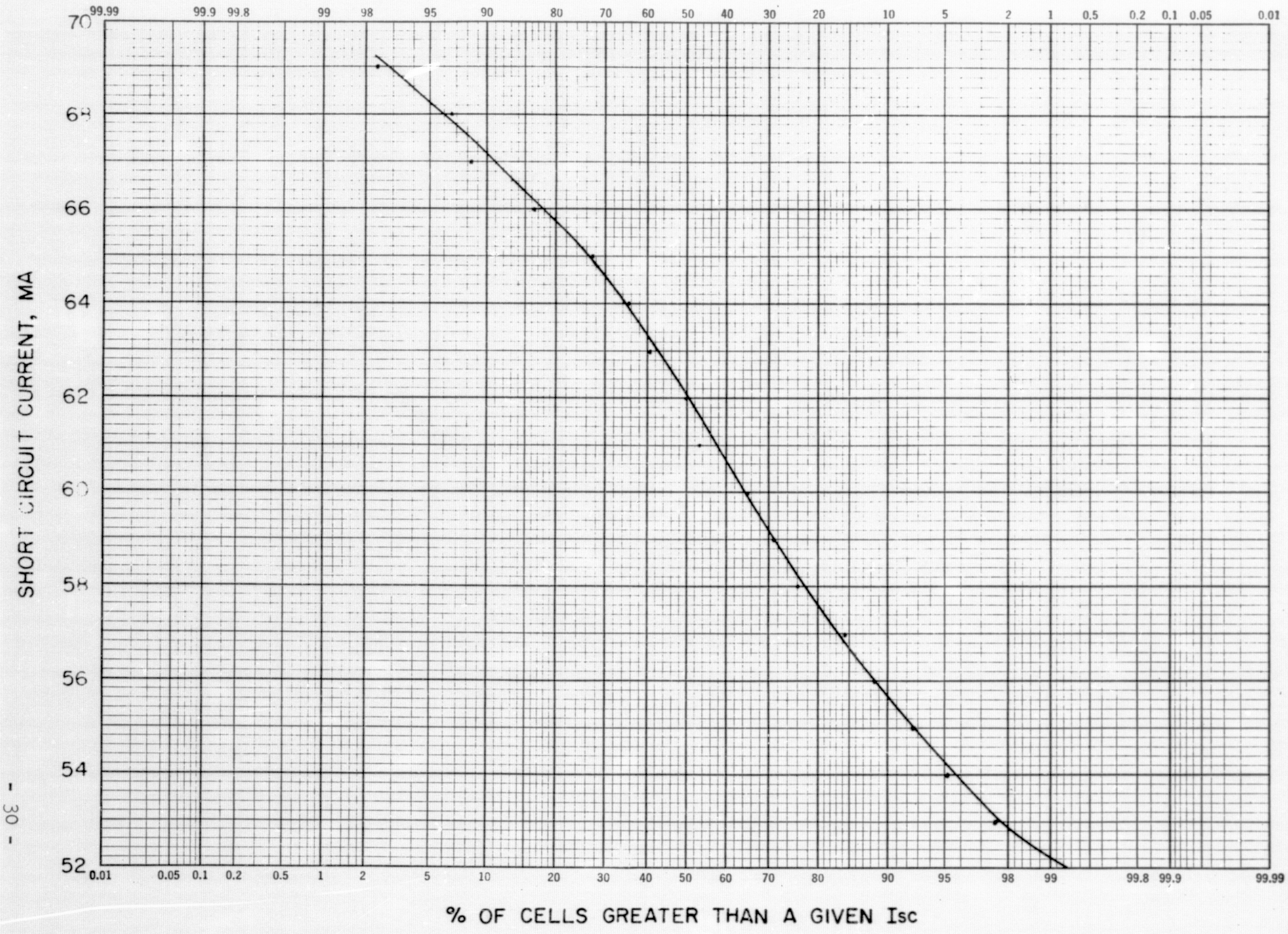


Figure 9. Short Circuit Current Distribution of Lithium Cells Fabricated for the First Shipment Lot. >100 ohm cm Czochralski Grown silicon, diffused 90 minutes, redistributed 60 minutes at 425°C. 120 cells measured in solar simulator at 140 mW/cm .

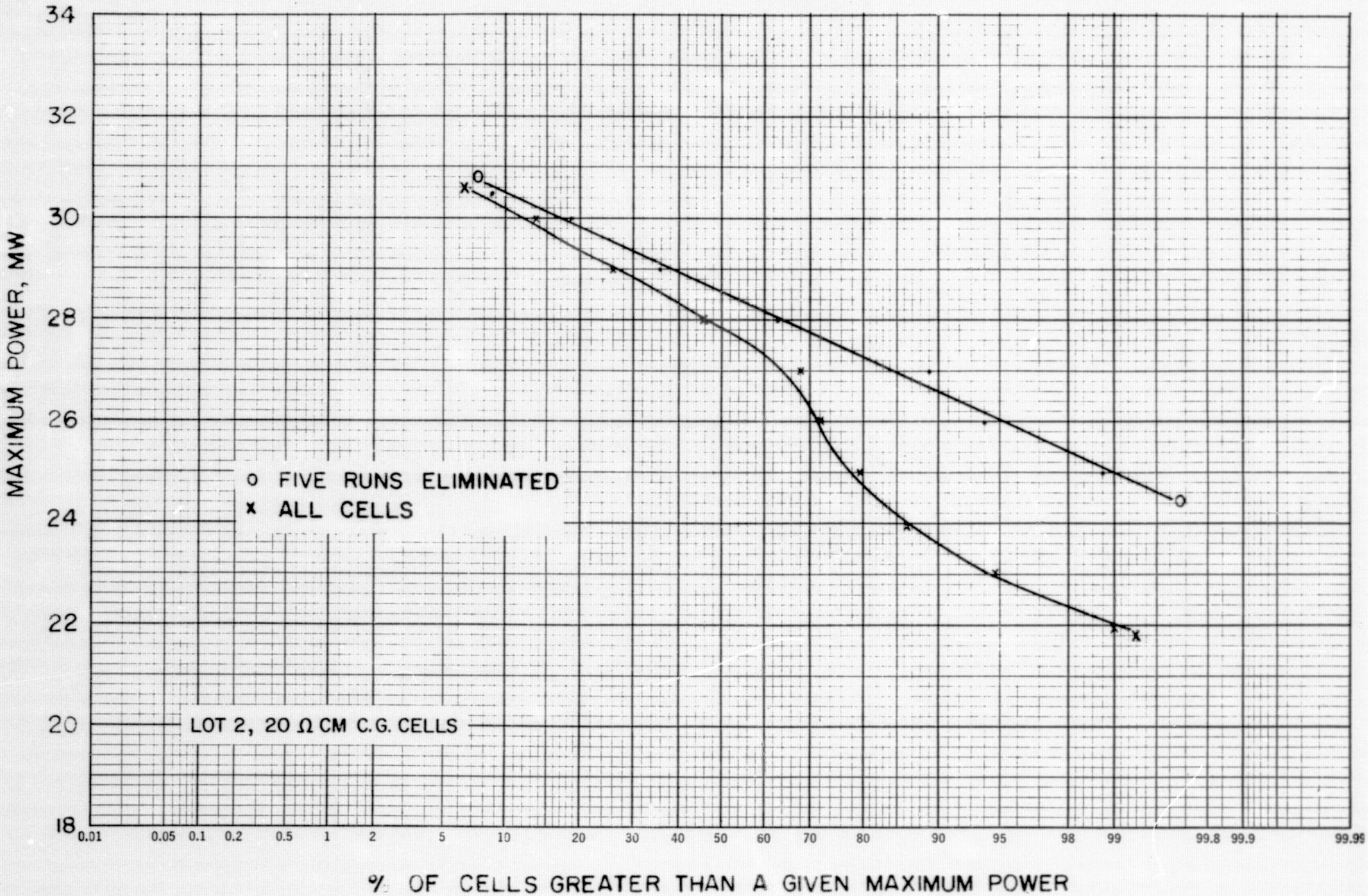


Fig. 10 Maximum Power Distribution of Lithium Cells Fabricated for the Second Shipment Lot. 20 ohm cm Czochralski Grown silicon, diffused 90 minutes, redistributed 60 minutes at 425°C. "0" = 81 cells, x = 113 cells. Measured in solar simulator at 140 mW/cm^2.

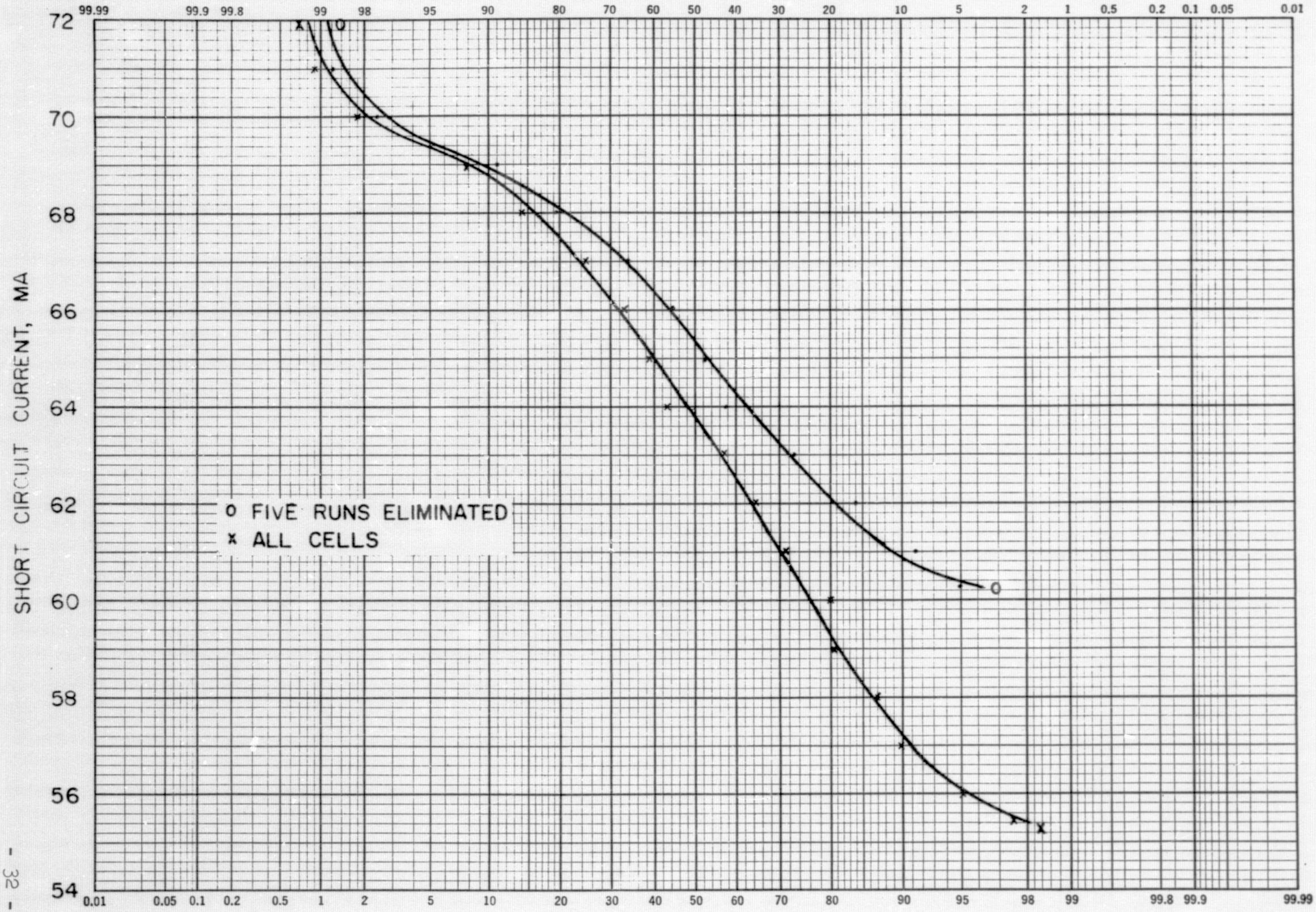


Figure 11. Short Circuit Current Distribution of Lithium Cells Fabricated for the Second Shipment Lot. 20 ohm cm Czochralski Grown silicon, diffused 90 minutes, redistributed 60 minutes at 425°C. "o"= 81 cells, x = 113 cells. Measured in solar simulator at 140 mW/cm^2.

would account for the improvement in the final output, however, it is a possibility. It was concluded that the primary variable affecting output and improving the distribution of the second lot of cells was the change in the boron diffusion process.

The third and fourth shipments consisted of 20 ohm cm Mon-x and 100 ohm cm float zone lithium cells, respectively; a 90 minute diffusion with 60 minutes redistribution at 425°C was used for both shipments. As seen in Figure 12, the maximum power distributions for the two shipments were very similar. Of the 117 Mon-x cells fabricated 5% were above 26.6 mW, 95% were above 21.1 and the maximum power 50% point was 23.6 mW; at these same points the group of seventy 100 ohm cm float zone cells had maximum powers of 26.0, 21.6, and 23.3 mW. With respect to the short circuit current (see Figure 13), the cells in both groups showed approximately the same distribution with 5% of the cells in both groups having short circuit currents of 63.1 mA or above. Below 60 mA the distribution of Mon-x cells was lower with 95% of the cells having short circuit currents of 53.6 mA or above, while for the 100 ohm cm float zone cells this 95% point was at 54.7 mA. The 50% point for the Mon-x cells was 57.2 mA, and for the 100 ohm cm float zone cells, 58.0 mA.

The fifth and sixth shipments consisted of 20 ohm cm float zone and 20 ohm cm crucible grown lithium cells, respectively. A 90 minute diffusion with 60 minutes redistribution was used for both lots; however, the float zone material was diffused at 350°C and the crucible grown silicon, at 450°C. The float zone cells were diffused at 350°C in order to evaluate the radiation recovery of cells with lower lithium concentrations and higher efficiencies. The 450°C lithium diffusion of the crucible grown silicon was selected in order to investigate the effect of higher lithium concentrations on the efficiency and radiation recovery of crucible grown lithium cells. This lot of crucible grown lithium cells provides a comparison with Lot 2 which consisted of crucible grown

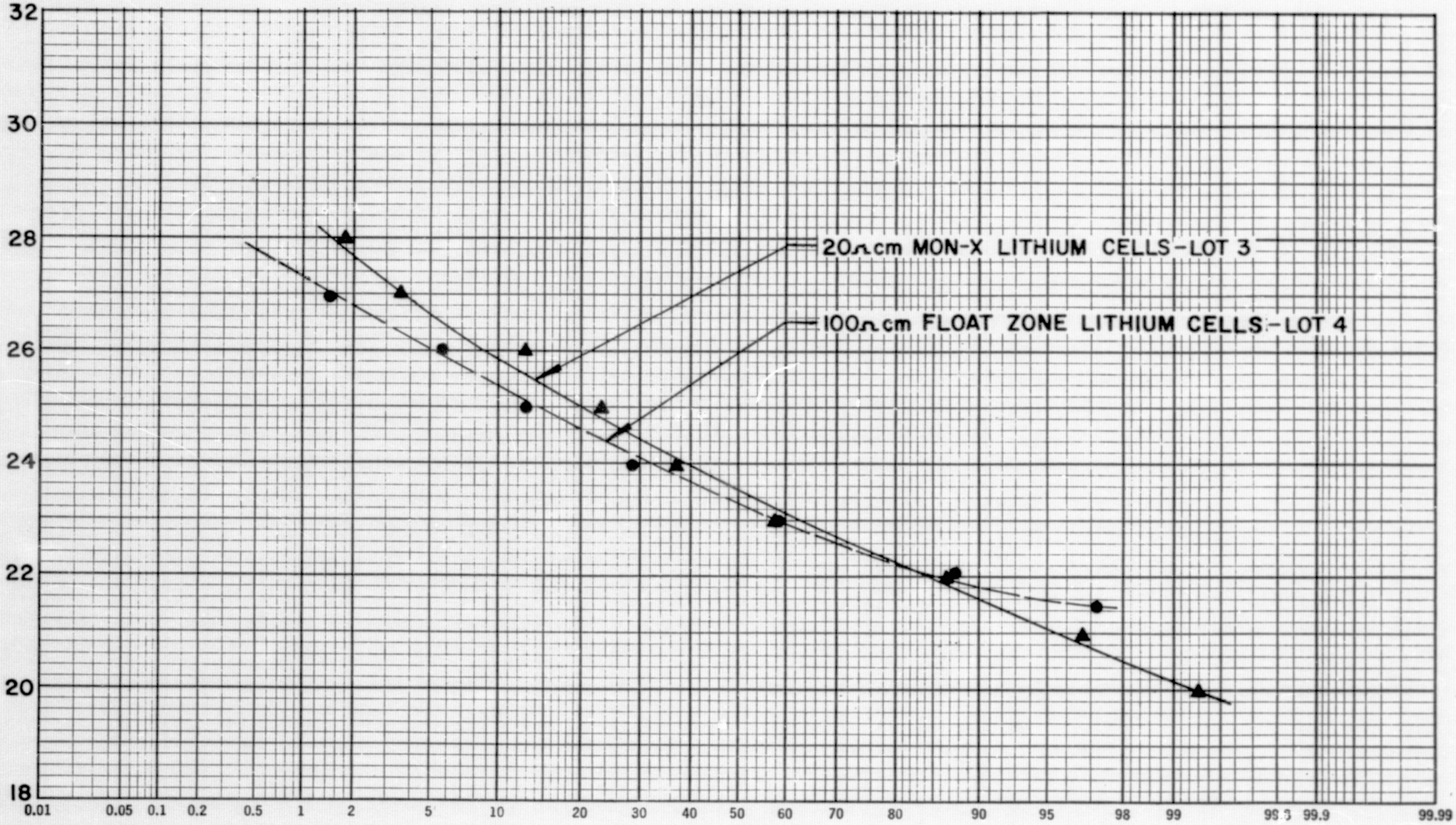


Figure 12. Maximum Power Distribution of Lithium Cells Fabricated for the Third and Fourth Lots; Third lot - 117 Mon-x cells, fourth lot - 70 float zone cells; both diffused 90 minutes, redistributed 60 minutes at 425°C; measured in solar simulator at 140 mW/cm^2.

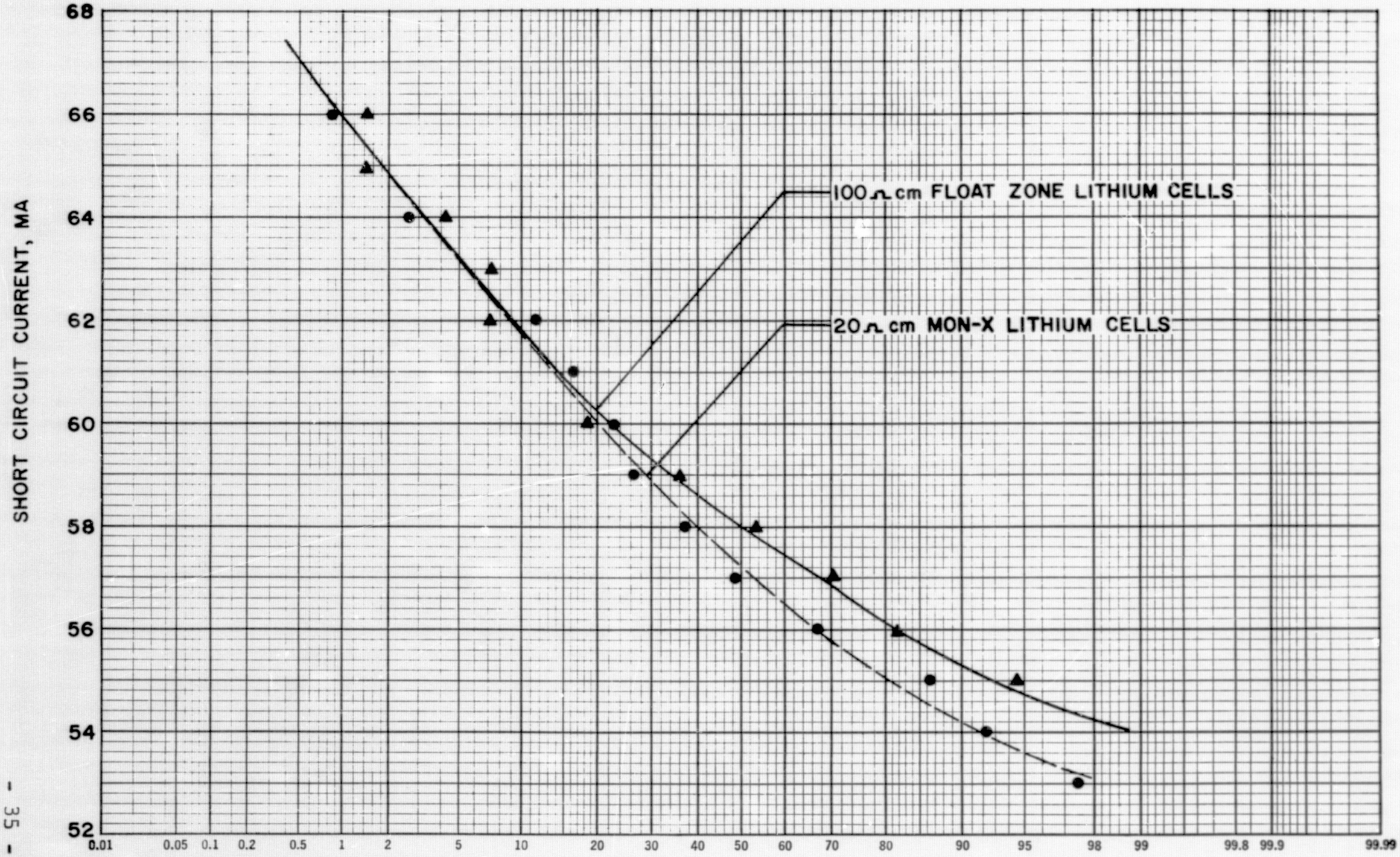


Figure 13. Short Circuit Distribution of Lithium Cells Fabricated for the Third and Fourth Lots; Third lot - 117 Mon-x cells, fourth lot - 70 float zone cells; both diffused 90 minutes, redistributed 60 minutes at 425°C; measured in solar simulator at 140 mW/cm^2.

lithium cells at 425°C. Figure 14 shows the maximum power distribution for 119 cells which were fabricated for Lot 5. The efficiencies on these cells were very good. Five percent of the cells had an output which was greater than 11.5% AMO efficiency or 31.2 mW; 50% of the cells were above 28.8 mW and 95% were above 26.4 mW. An efficiency of 11% was obtained for 24% of the cells and 86% of the cells had efficiencies greater than 10%. The efficiency of 50% of this group of cells was 10.5% or greater which was much higher than for float zone cells lithium diffused at 425°C. The short circuit distribution for these Lot 5 cells is shown in Figure 15 . Five percent of the cells were above 76 mA, 50% were above 72 mA, and 95% were above 64 mA. These cells have relatively low lithium concentrations; however, they should not be completely eliminated for potential use in a radiation environment since it may be demonstrated that these cells will be radiation resistant in a low level radiation environment or recover satisfactorily at a slightly elevated temperature.

Figures 16 and 17 show the maximum power and short circuit current distributions for the 98 cells fabricated for Lot 6. These distribution curves are not continuous since there are two distinct distributions in the total population. The lower distribution shows the characteristics of approximately the first 80 cells made. From this group of cells one would conclude that the increased lithium concentration obtained in a 450°C diffusion resulted in outputs significantly lower than those obtained in 425°C diffusions. However, toward the end of the fabrication period, additional material was needed, and some additional blanks from another silicon ingot (#2)* were used. These new blanks from ingot 2 and a few of the blanks left from the silicon ingot (#1)* used for the 80 cells mentioned above were boron diffused on the same day, although not in the same diffusion. The lithium cells fabricated from ingot #2

*Arbitrary numbers used only for clarity.

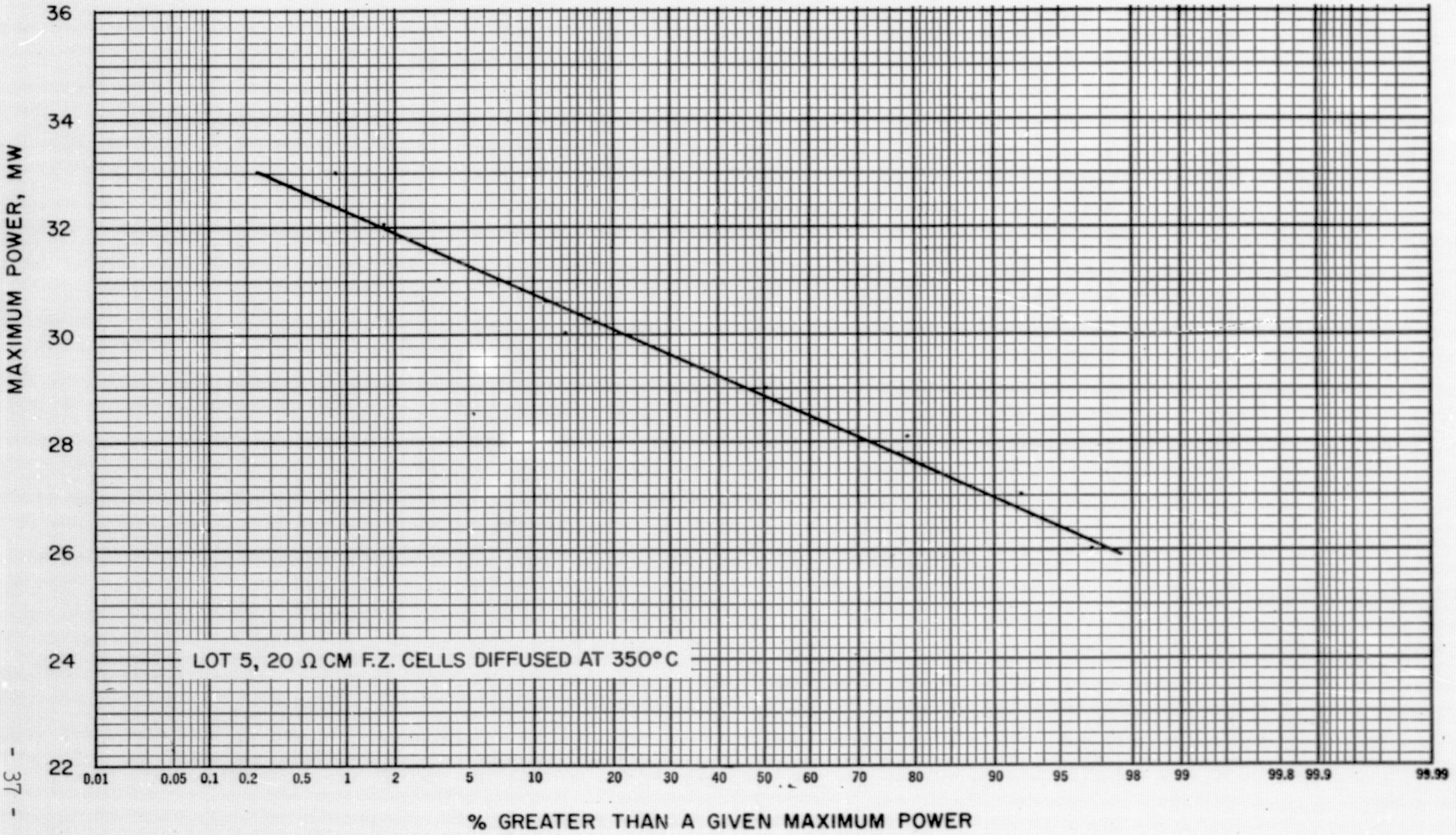


Figure 14. Maximum Power Distribution of Lithium Cells Fabricated for the Fifth Lot (119 cells); 20 ohm cm float zone cells, Lithium Diffused 90 minutes and redistributed 60 minutes at 350°C; measured in solar simulator at 140 mW/cm^2.

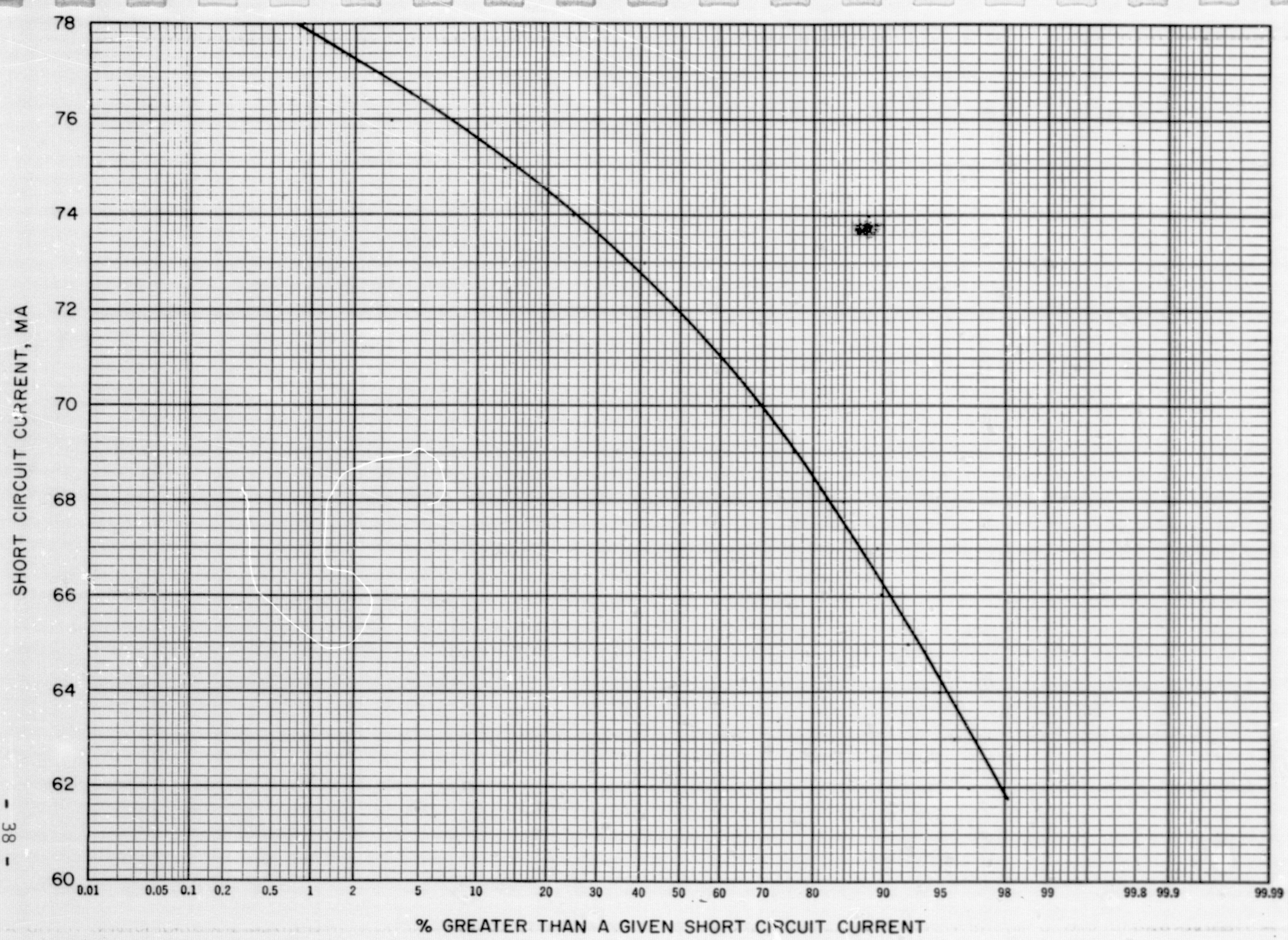


Figure 15. Short Circuit Current Distribution of Lithium Cells Fabricated for the Fifth Lot (119 cells); 20 ohm cm Float Zone Cells, Lithium Diffused 90 Minutes and Redistributed 60 Minutes at 350°C; measured in Solar Simulator at 140 mW/cm^2

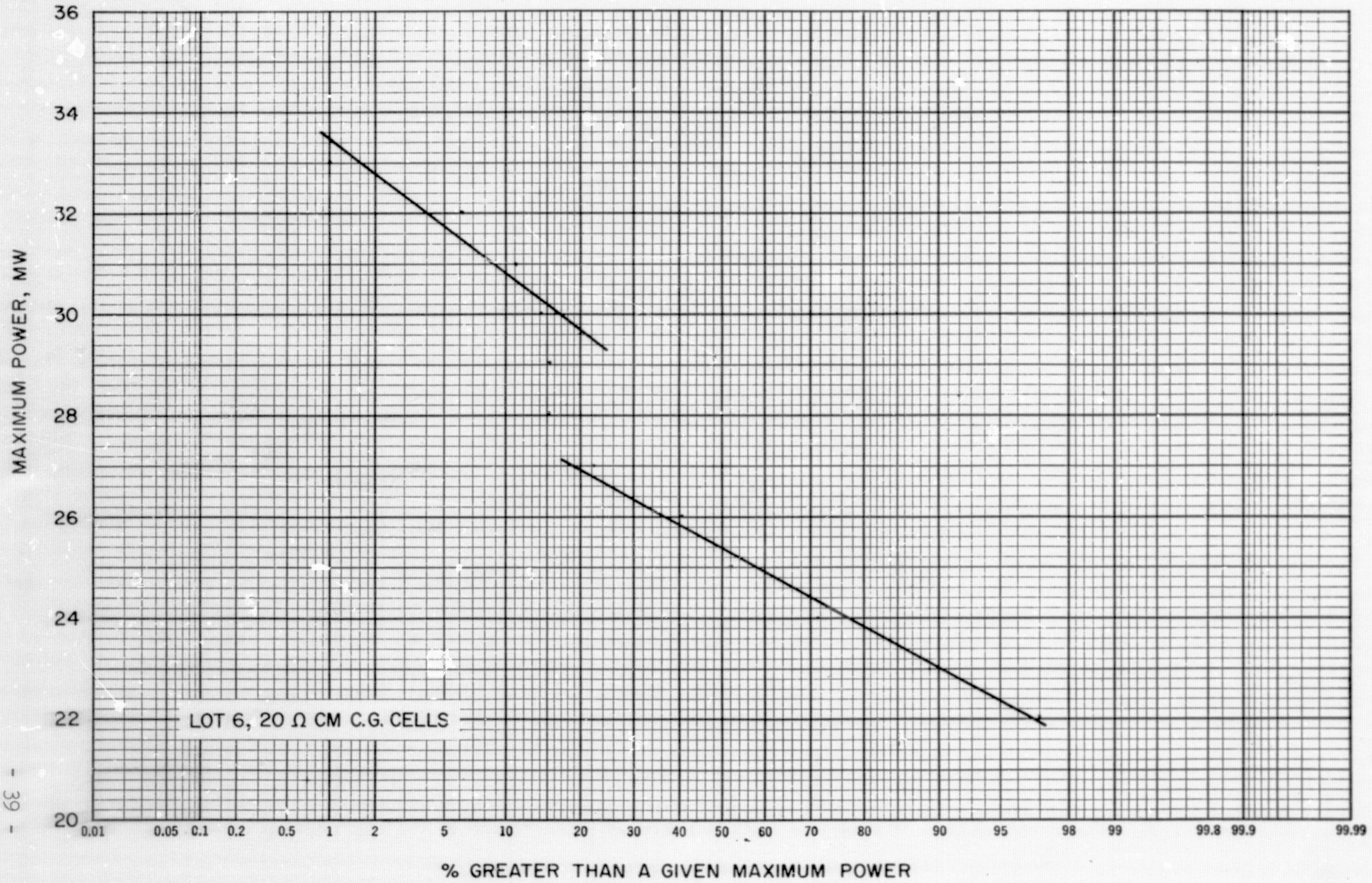


Figure 16 Maximum Power Distribution of Lithium Cells Fabricated for the Sixth Lot (99 cells); 20 ohm cm Crucible Grown cells, lithium diffused 90 minutes and redistributed 60 minutes at 450°C; measured in solar simulator at 140 mW/cm^2.

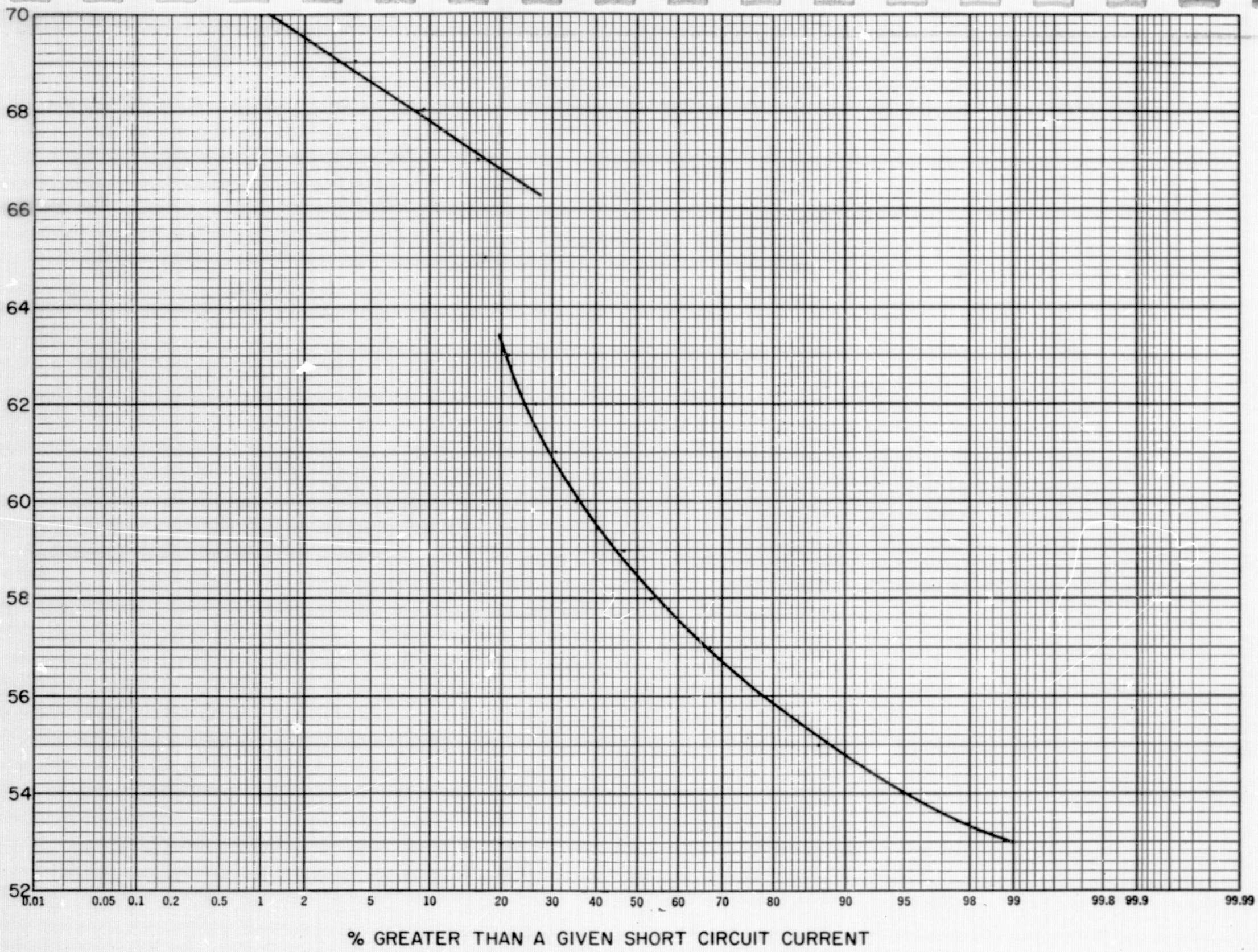


Figure 17. Short Circuit Current Distribution of Lithium Cells Fabricated for the Sixth Lot (99 cells); 20 ohm cm Crucible Grown Cells, Lithium Diffused 90 Minutes and Redistributed 60 Minutes at 450°C; Measured in Solar Simulator at 140 mW/cm^2

are those shown in the upper distribution in both Figures 16 and 17. These results strongly indicate the possibility of material variations; however, since blanks from the two different ingots were not included in the same boron diffusion, there is a slight possibility that the difference could be associated with the boron diffusions.

The seventh lot was fabricated from 20 ohm cm Lopex silicon using a 90 minute lithium diffusion and 60 minute redistribution at 425°C. The cells showed a very wide range in open circuit voltage - from 550-610 mV, which was unusual for the diffusion parameters used. These diffusion parameters typically result in open circuit voltages from 550 to 580 mV (with 580 mV being exceptionally high) for cells fabricated from float zone silicon. Past work with Lopex silicon has resulted in cells with open circuit voltages from 550 to 580 mV, indicating that reduction in the number of dislocations did not affect the open circuit voltage. However, the open circuit voltage of lithium cells is affected by oxygen content, since the use of crucible grown silicon, which has a much higher oxygen content than that specified for either float zone or Lopex silicon, results in lithium cells with open circuit voltages of 580 to 610 mV. Since Lot 7 consisted of Lopex silicon lithium cells which also had open circuit voltages in this high range (as well as lower) it may be an indication that the oxygen content varies significantly in Lopex silicon. Due to the extremely high open circuit voltages, many of the cells had outputs as high as crucible grown lithium cells. The maximum power (see Figure 18) was 28.4 mW or above for 50% of the cells, while 5% of the cells were above 31.5 mW and 95% of the cells were above 24.7 mW. In the case of the short circuit current, shown in Figure 19, 5% of the cells were above 72.6 mA, 50% were above 66.7 mA, and 95% were above 62.9 mA.

Lot 8 cells were fabricated from 100 ohm cm float zone silicon with

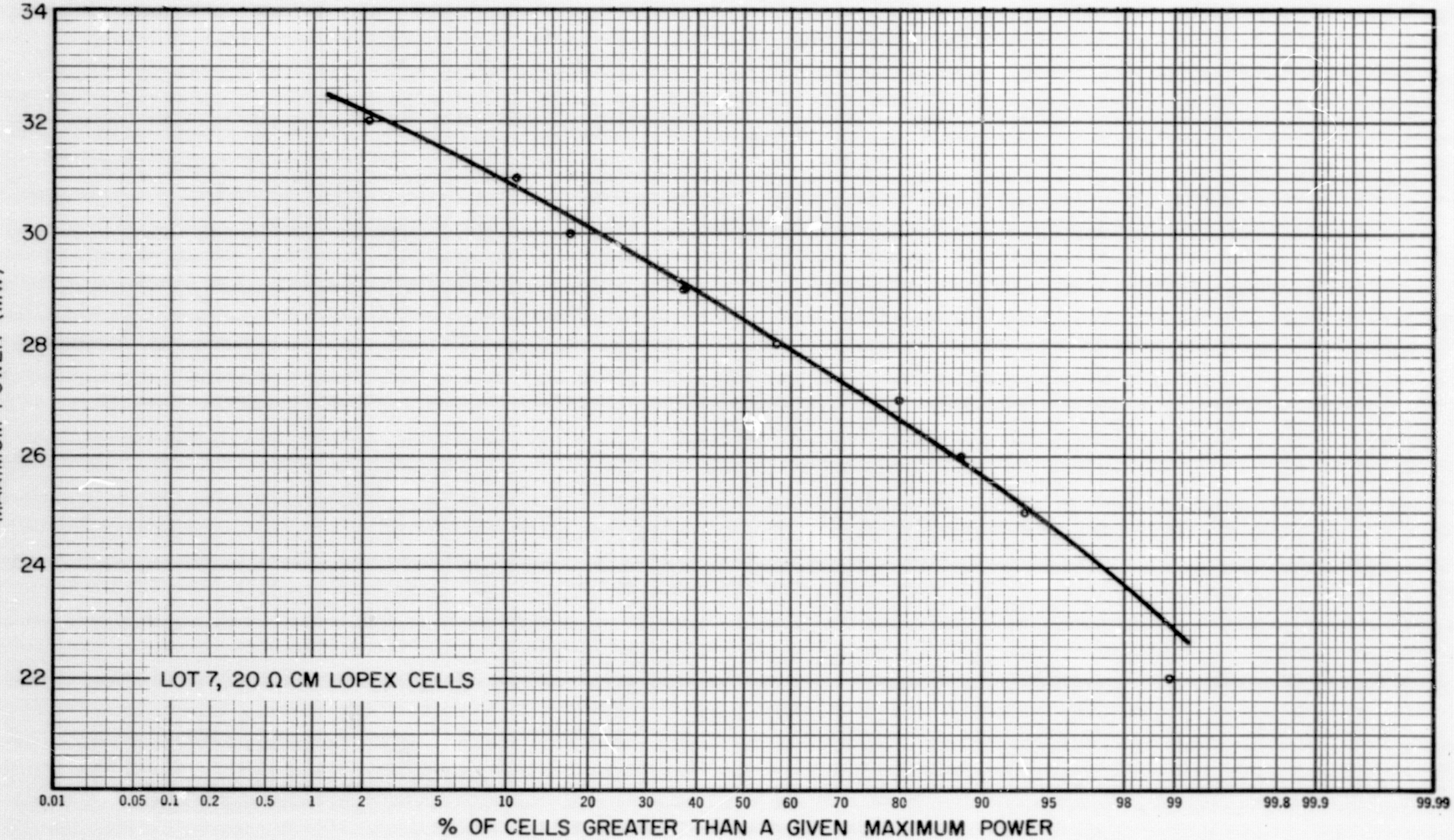


Figure 18. Maximum Power Distribution of Lithium Cells Fabricated for the Seventh Lot (92 cells); 20 ohm cm Lopex cells, lithium diffused 90 minutes and redistributed 60 minutes at 425°C; measured in solar simulator at 140 mW/cm^2.

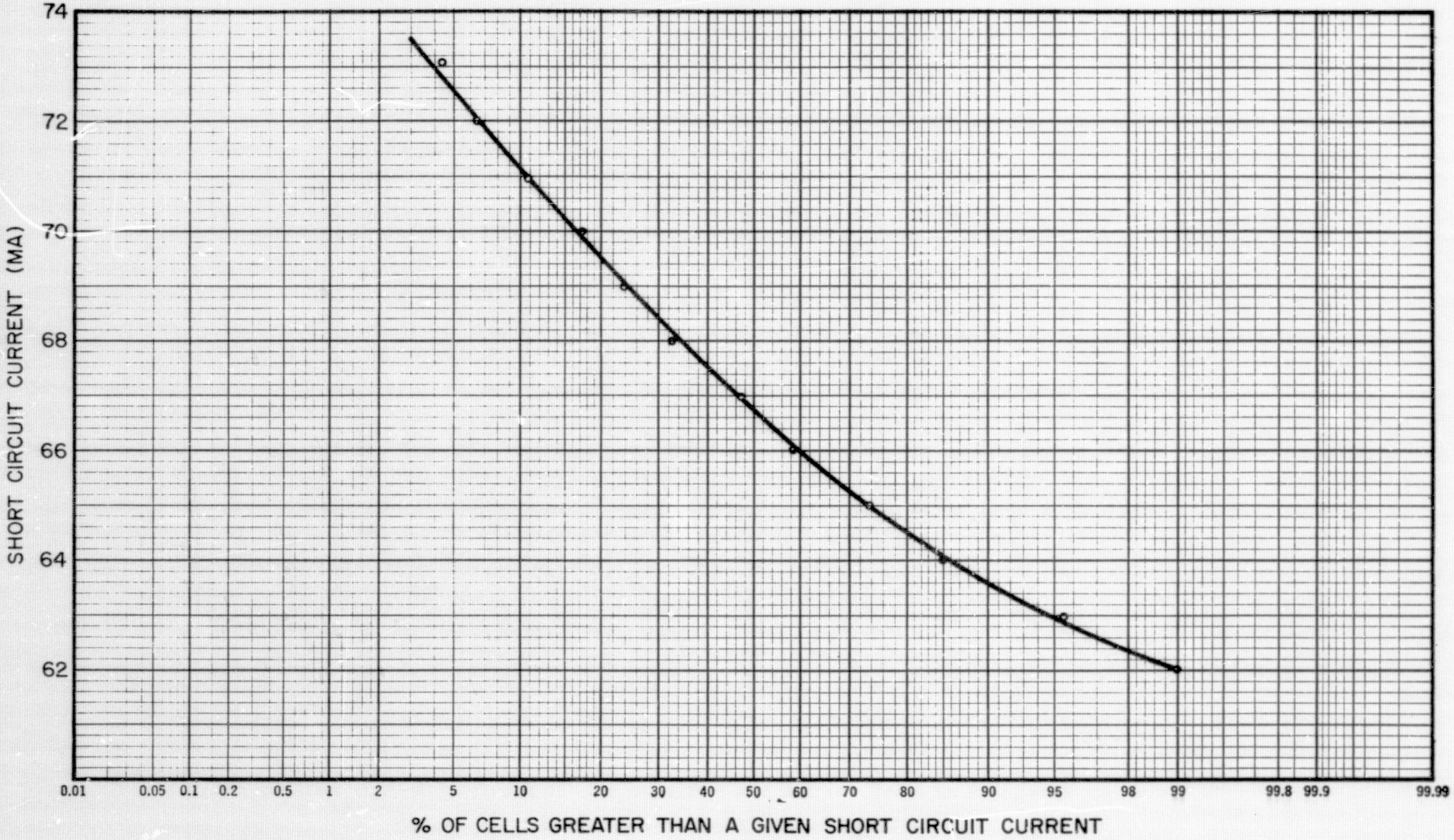


Figure 19. Short Circuit Current Distribution of Lithium Cells Fabricated for the Seventh Lot (92 cells); 20 ohm cm Lopex cells, lithium diffused 90 minutes and redistributed 60 minutes at 425°C; measured in solar simulator at 140 mW/cm^2.

a special diffused phosphorus region at the junction and a lithium diffusion of 90 minutes with 60 minutes redistribution at 425°C. The processing of these cells included a phosphorus diffusion as well as the boron and lithium diffusions. The major problem in the fabrication of these cells was obtaining a good boron diffusion on top of the phosphorus layer. In general the phosphorus diffused surface was very rough and non-uniform in appearance after it came out of boron diffusion. This probably indicated an uneven and possibly discontinuous boron layer which would account for the shunting problems encountered in the fabricated cells. The cells were processed in several groups that were characterized by different etch steps. The first group of cells was only etched in HF between the phosphorus and boron diffusion thus leaving a very high phosphorus surface concentration. This group had a high percentage of gross shunting. This shunting was not localized at the edges since it could not be improved by tape, trimming, and etching the edges. In addition to being etched in HF, the second group of cells was etched 15 seconds in a hot dilute NaOH solution. The shunting was not as serious for this group; however, it was still an undesirable value. For this reason a longer NaOH etch was used. This resulted in a reduced phosphorus concentration; however, the problems with the boron diffusion were eliminated. The cells came out of boron diffusion with a smooth, unblemished surface and none of the cells were seriously shunted. The maximum power and short circuit current distributions for these cells are shown in Figures 20 and 21 . Only 62 cells were used to obtain these distributions since the remainder of the cells were from the first group that were badly shunted. The maximum power 50% point was 23.7 mW, 5% of the cells were above 27.8 mW and 95% were above 21.0 mW. The same points on the short circuit current distribution were 60.3 mA, 66.9 mA, and 53.6 mA.

Lot 9 consisted of 20 ohm cm float zone cells lithium diffused 90 minutes and redistributed 60 minutes at 425°C. The output of

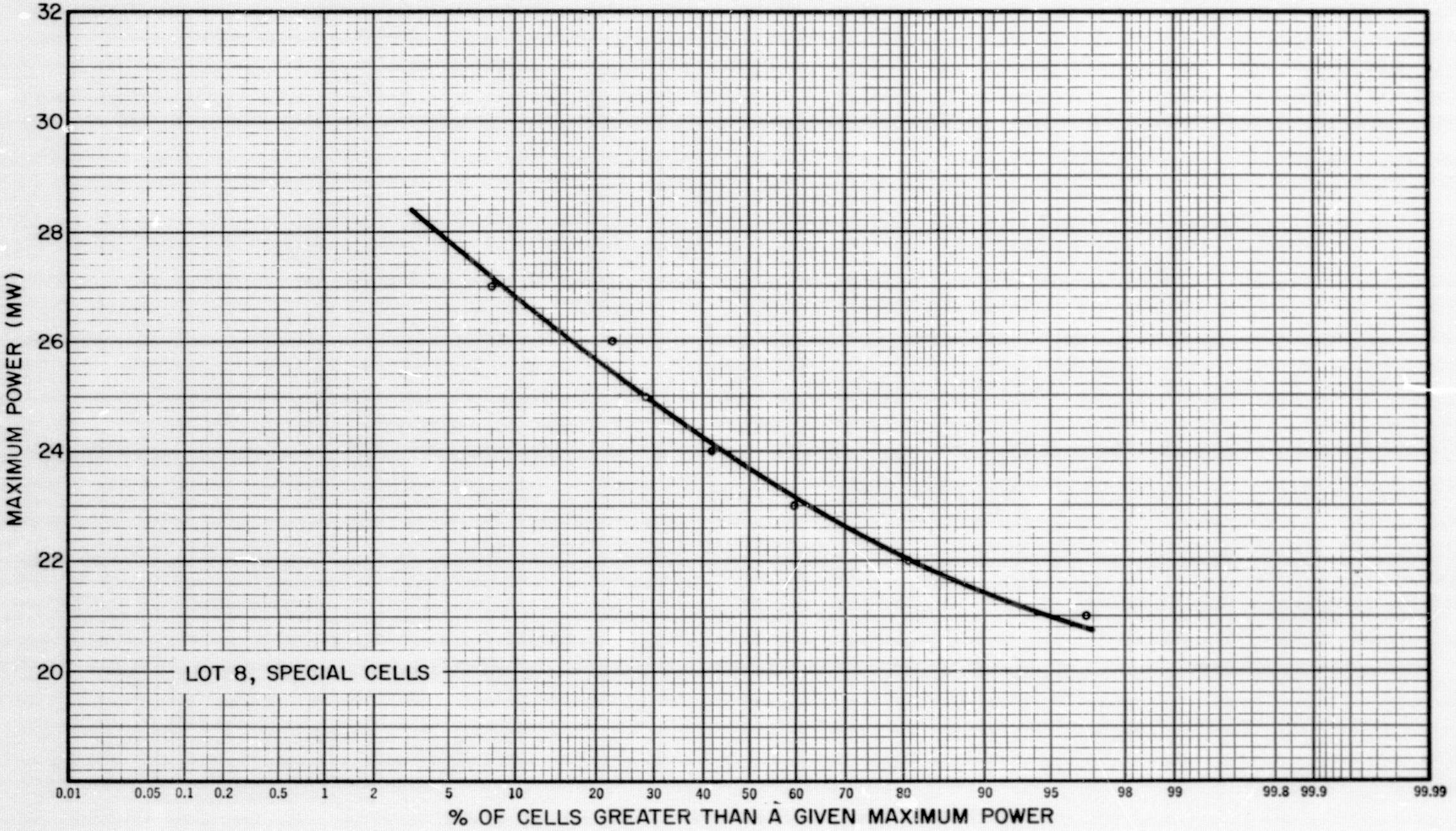


Figure 20. Maximum Power Distribution of Lithium Cells Fabricated for the Eighth Lot (62 cells); 100 ohm cm float zone cells, lithium diffused 90 minutes and redistributed 60 minutes at 425°C; measured in solar simulator at 140 mW/cm^2.

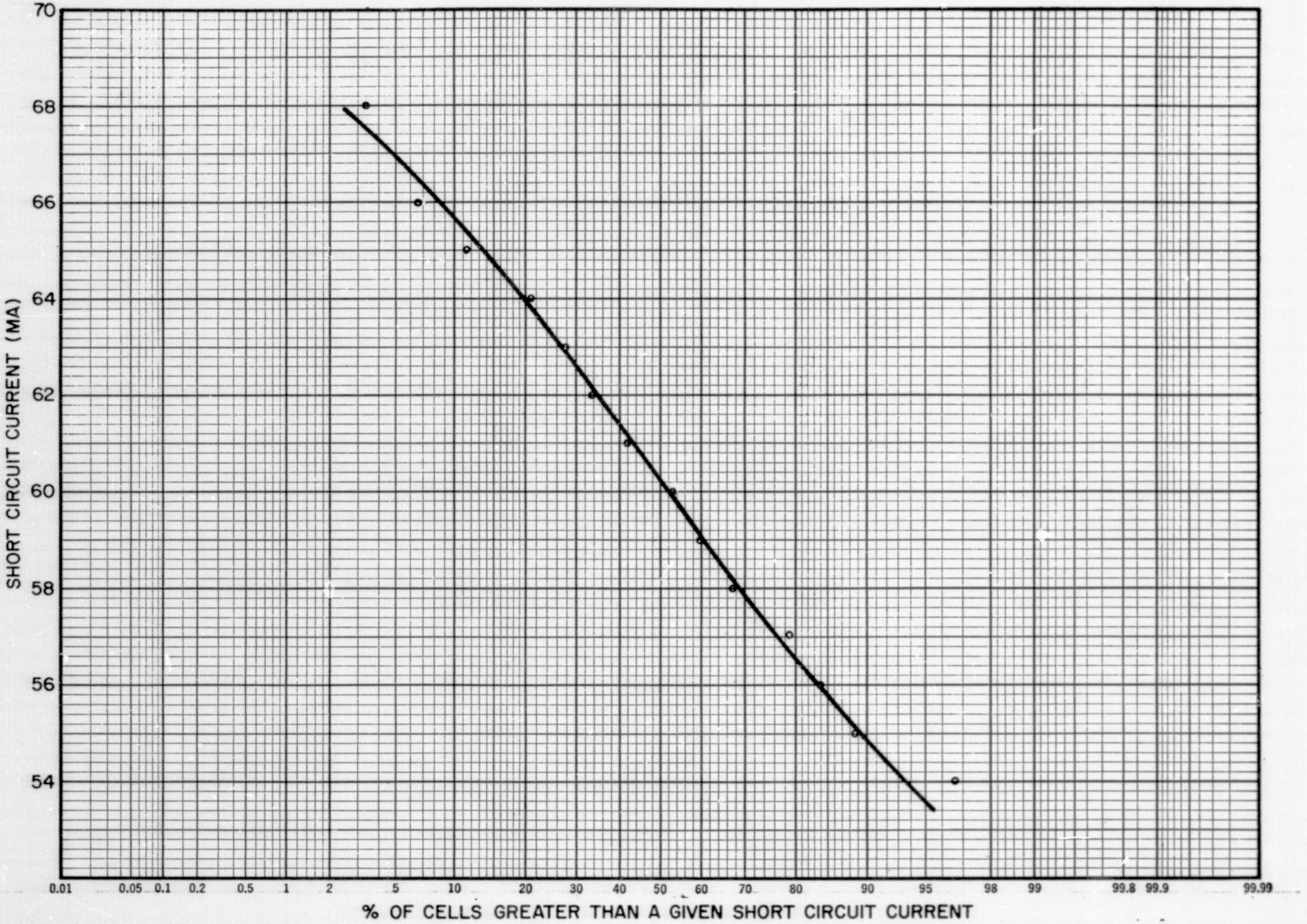


Figure 21. Short Circuit Current Distribution of Lithium Cells Fabricated for the Eighth Lot (62 cells); 100 ohm cm float zone cells, lithium diffused 90 minutes and redistributed 60 minutes at 425°C; measured in solar simulator at 140 mW/cm^2.

these cells was not as high as that of crucible grown lithium cells; however, the maximum power distribution was quite narrow (see Figure 22). The output was 27.1 mW or greater for 50% of the cells, with 5% of the cells above 29.0 mW and 95% of the cells above 25.2 mW. The maximum power range for 90% of the cells was only 3.8 mW. The short circuit current distribution, Figure 23, with a 7.3 mA spread for 90% of the cells, compared to 9.2 to 14.6 mA spreads for the other lots, was also very narrow. The short circuit current was 62.9 mA or greater for 50% of the cells, with 5% of the cells above 67.1 mA and 95% above 59.8 mA.

The lithium cells for Lot 10 were fabricated from 20 ohm cm Czochralski grown silicon with a lithium diffusion of 90 minutes and a redistribution of 60 minutes at 425°C. The efficiency of these cells was good; in fact, the maximum power distribution as shown in Figure 24 was the highest of the cntire ten lots. The cell output was above 29.0 mW for 50% of the cells, with 95% of the cells above 26.0 mW and 5% of the cells above 32.0 mW. Considering the short circuit current, 5% of the cells were above 70.5 mA, 50% were above 65.0 mA, and 95% were above 59.6 mA (see Figure 25).

The same type material and diffusion parameters were used for both Lots 2 and 10 and this provided an opportunity to compare cells made at widely different time periods. Figure 26 compares the maximum power distributions of the two lots. Both distributions are shown for Lot 2; the lower one includes all the cells and the upper distribution has the five consecutive low output diffusion runs or thirty-two cells eliminated. The distribution for Lot 10 is slightly above the higher distribution for Lot 2 and it correlates closely to the higher Lot 2 distribution. In other words, Lot 10 has shown that outputs as high as those in the higher distribution for Lot 2 can be obtained reproducibly.

A comparison of float zone (Lot 9) and crucible grown lithium cells (Lot 10) both fabricated from 20 ohm cm material and subjected to the same lithium diffusion conditions is shown in Figure 27. The distribution for the float zone cells is much narrower and therefore there

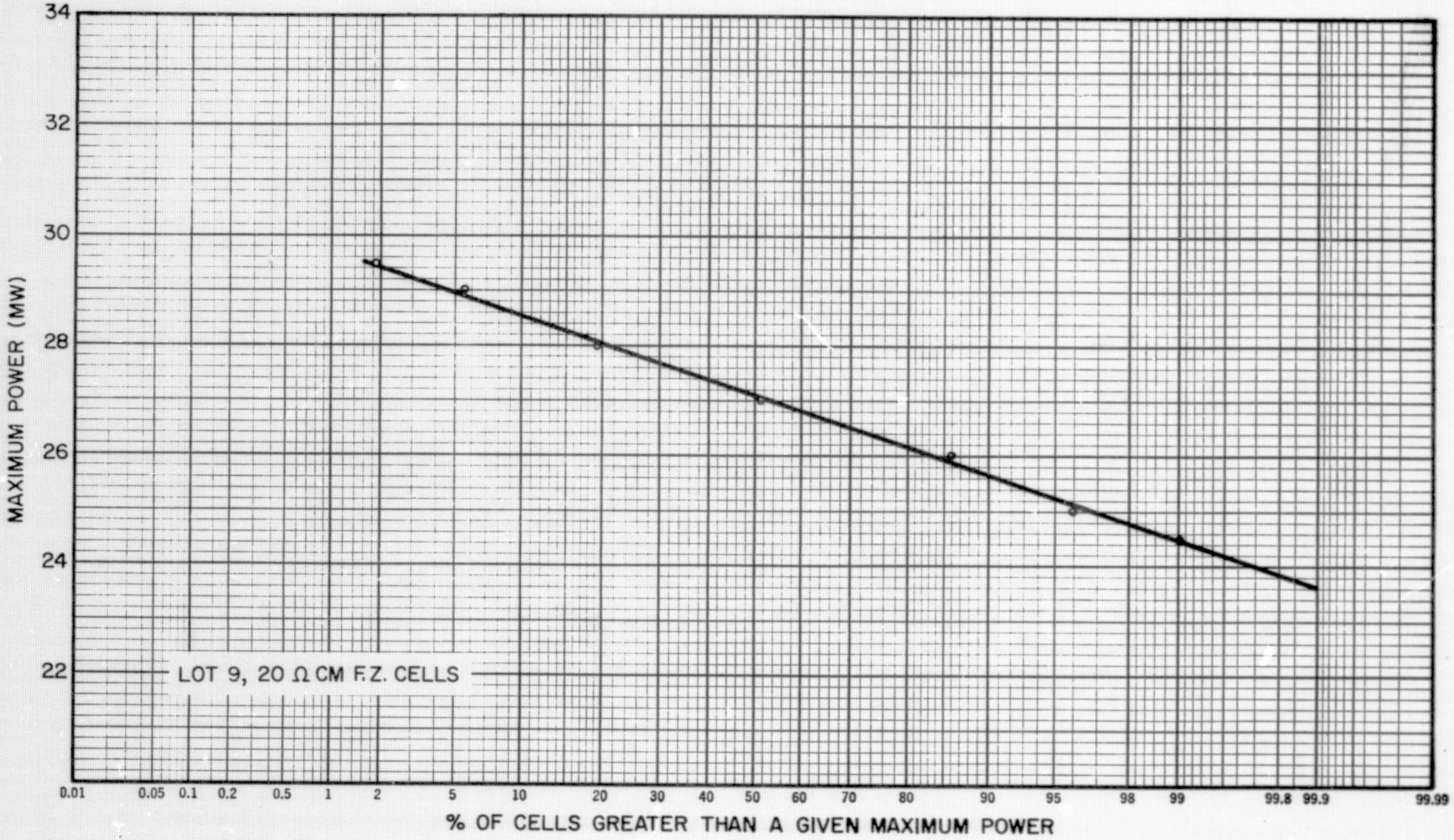


Figure 22. Maximum Power Distribution of Lithium Cells Fabricated for the Ninth Lot (109 cells); 20 ohm cm float zone cells, lithium diffused 90 minutes and redistributed 60 minutes at 425°C; measured in solar simulator at 140 mW/cm^2.

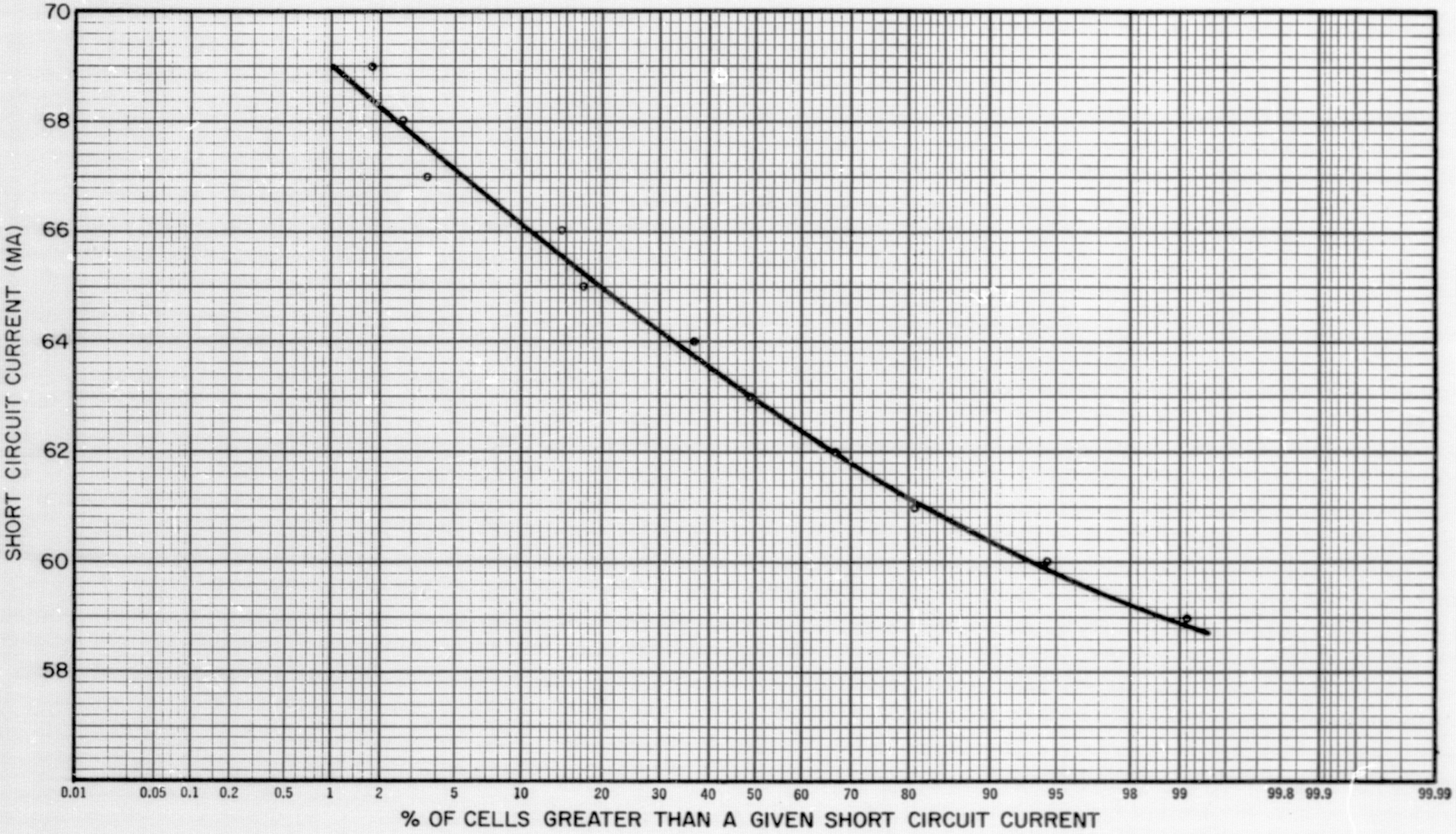


Figure 23. Short Circuit Current Distribution of Lithium Cells Fabricated for the Ninth Lot (109 cells); 20 ohm cm float zone cells, lithium diffused 90 minutes and redistributed 60 minutes at 425°C; measured in solar simulator at 140 mW/cm^2.

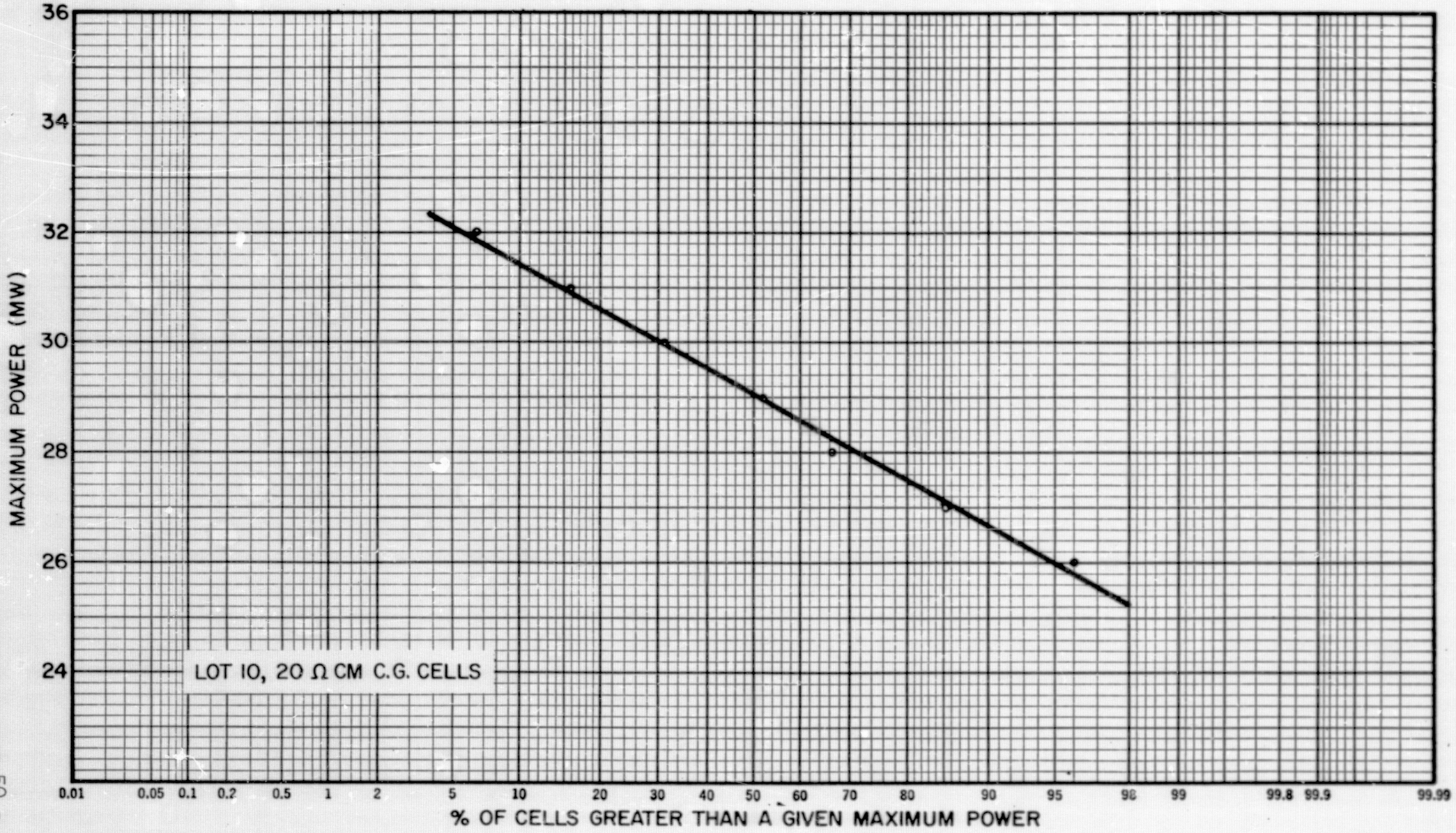


Figure 24. Maximum Power Distribution of Lithium Cells Fabricated for the Tenth Lot (113 cells); 20 ohm cm Crucible Grown cells, lithium diffused 90 minutes and redistributed 60 minutes at 425°C; measured in solar simulator at 140 mW/cm^2.

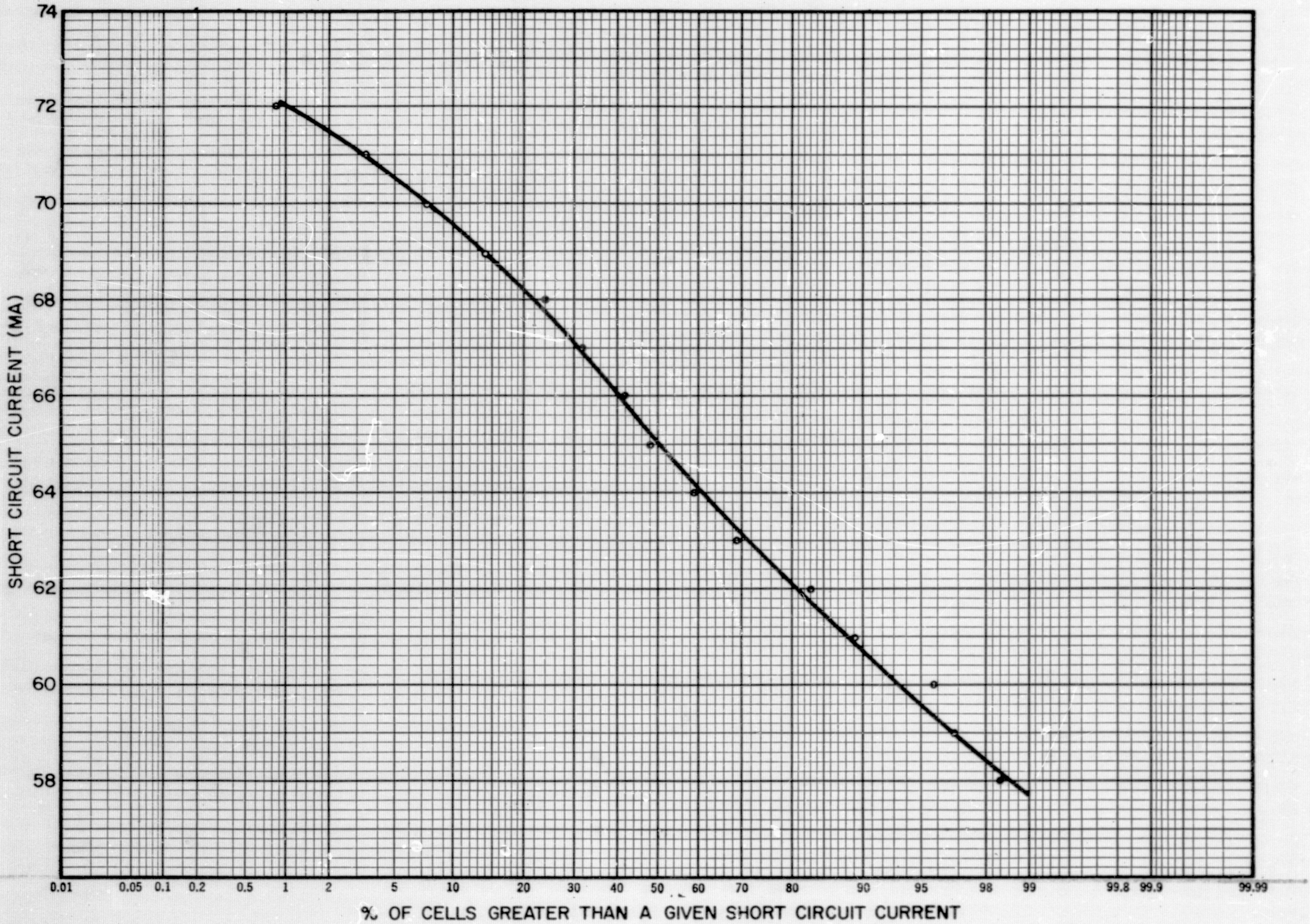


Figure 25. Short Circuit Current Distribution of Lithium Cells Fabricated for the Tenth Lot (113 cells); 20 ohm cm Crucible Grown cells, lithium diffused 90 minutes and redistributed 60 minutes at 425°C; measured in solar simulator at 140 mW/cm^2.

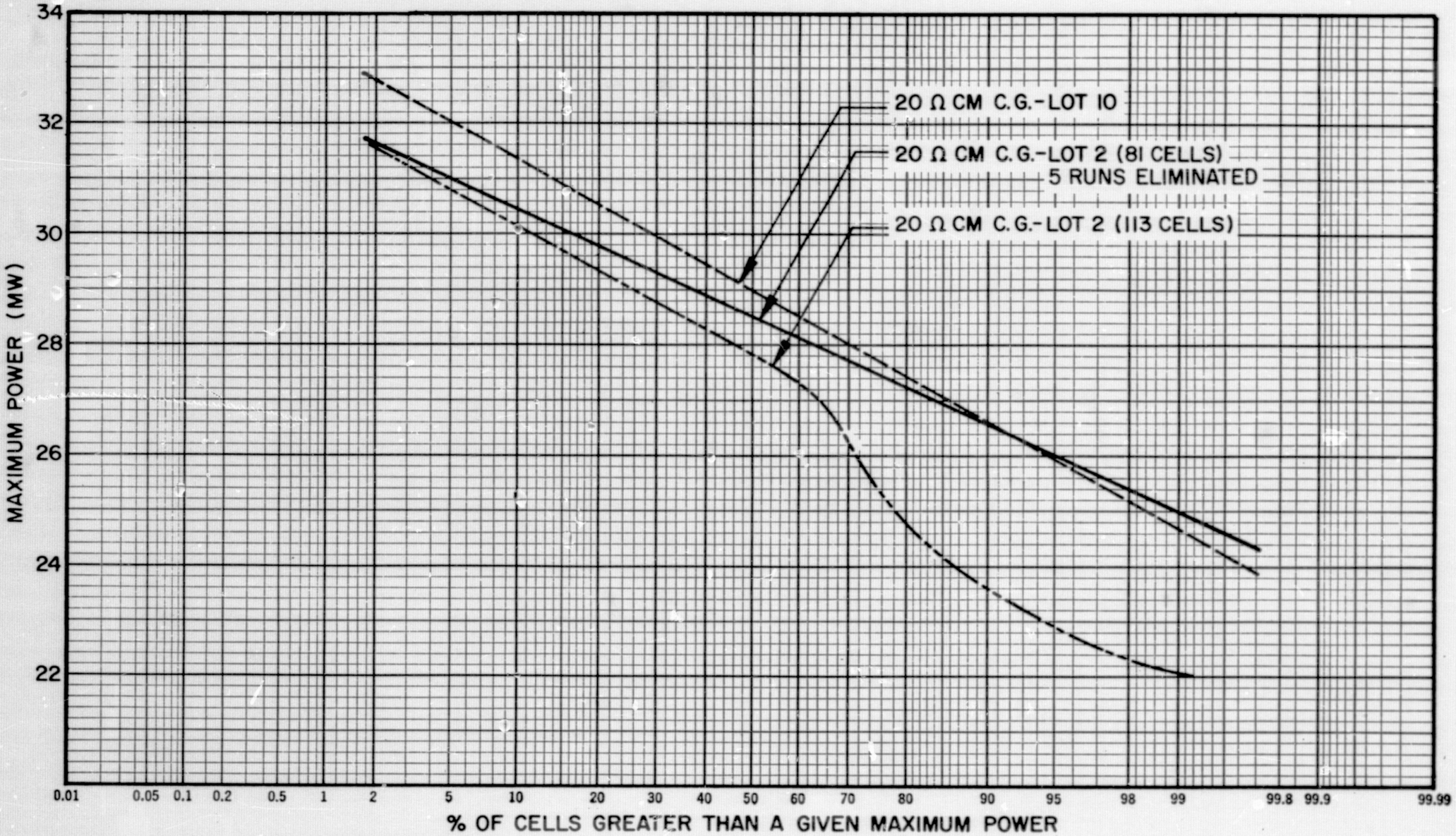


Figure 26. Comparison of Maximum Power Distributions of Two Different Lots of Crucible Grown Lithium Cells. Both groups of cells diffused 90 minutes, redistributed 60 minutes at 425°C; measured in solar simulator at 140 mW/cm^2.

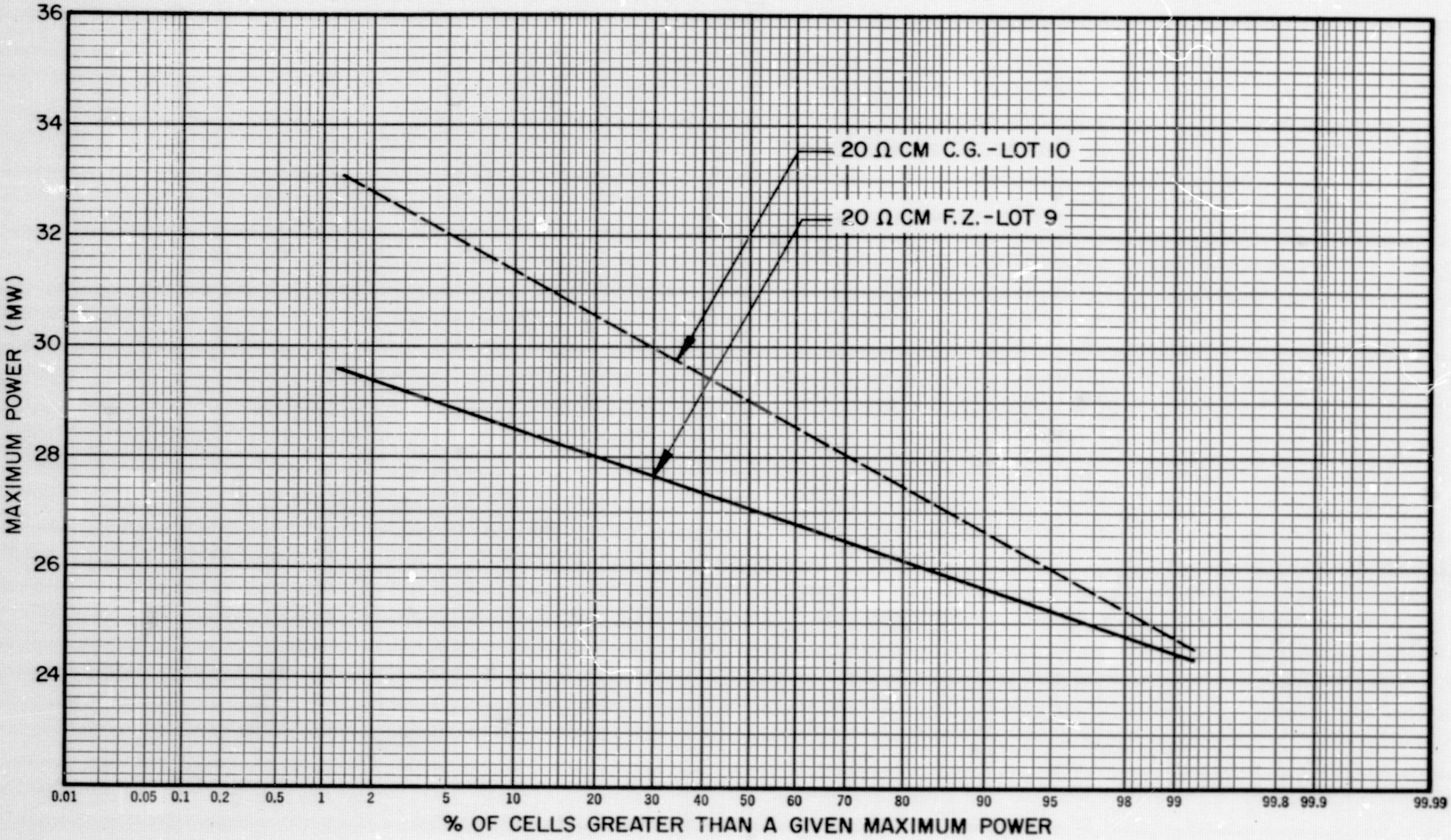


Figure 27. Comparison of Maximum Power Distributions of Crucible Grown and Float Zone Lithium Cells. Both groups diffused 90 minutes, redistributed 60 minutes at 425°C; measured in solar simulator at 140 mW/cm^2.

was only .8 mW difference between the maximum power for the 95% point for both types of cells. However, the maximum power for 50% of the float zone cells was 27.1 mW or greater which was 1.9 mW lower than the 29.0 mW for the crucible grown cells. The maximum power for the top 5% of the float zone cells was 29.0 mW or greater, whereas the top 5% of the crucible grown cells was above 32.0 mW. This shows that although the low output float zone and crucible grown lithium cells are very similar in output, the average crucible grown lithium cell is 2 mW higher than the average float zone lithium cell.

Outputs comparable to crucible grown lithium cells can be obtained from float zone lithium cells if the lithium concentration is reduced. Figure 28 shows maximum power distributions for crucible grown cells lithium diffused at 425°C and float zone cells diffused at 350°C. The top 5% of the crucible grown lithium cells are slightly higher (.7 mW); however this difference decreases and the distributions cross so that at the lower end of the distributions the float zone lithium cells have slightly higher outputs.

Table V summarizes the material, diffusion and output parameters of all ten lots. The 90 minute diffusion time and 60 minute redistribution was kept constant for all ten lots. A diffusion temperature of 425°C was used for eight lots; 350°C and 450°C were used for the other two lots. The maximum power points listed show that the best outputs at the 50% yield point (essentially the mean value) for cells diffused at 425°C were about 28.0-29.0 mW and were obtained with Lots 2, 7, and 10. Lots 2 and 10 were made up with crucible grown lithium cells and Lot 7 consisted of Lopex lithium cells. An output of 28.8 mW was also obtained with float zone lithium cells when the diffusion temperature was lowered to 350°C. Earlier work by this laboratory has shown that higher short circuit currents are obtained with lower diffusion temperatures. This was again supported by Lot 5, which was diffused at 350°C. The short circuit current for this lot was 71.9 mA

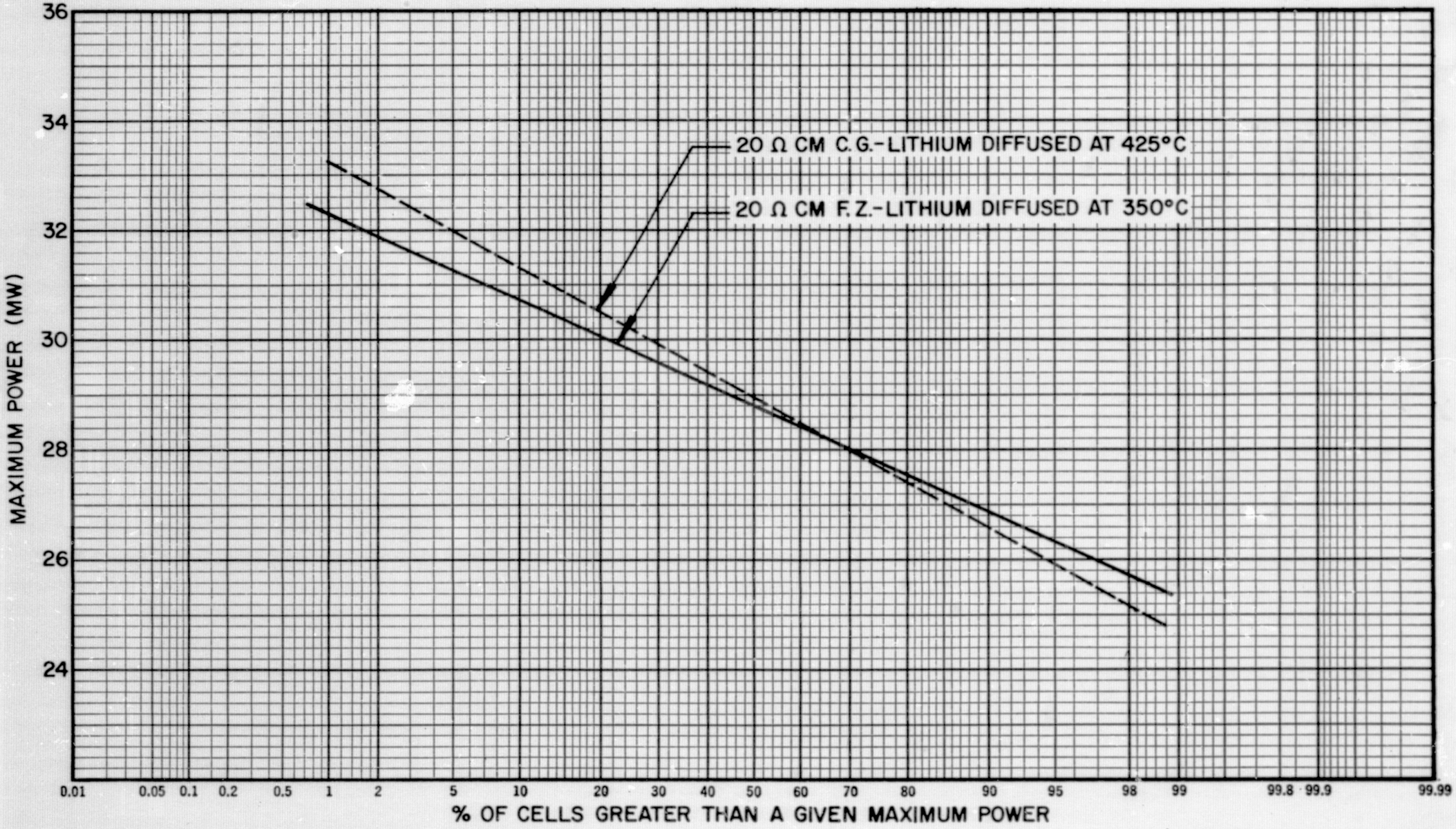


Figure 28. Comparison of Maximum Power Distribution of Crucible Grown and Float Zone Lithium Cells. Both groups diffused 90 minutes and redistributed 60 minutes; measured in solar simulator at 140 mW/cm^2.

SUMMARY OF ALL TEN LOTS

Shipment Lot	Material Type and Resistivity	Diffusion/ Redistrib. min.	Temp °C	Maximum Power, mW			Short Circuit Current, mA		
				5% of Cells ≥	50% of Cells ≥	95% of Cells ≥	5% of Cells ≥	50% of Cells ≥	95% of Cells ≥
1	>100 ohm cm CG	90/60	425	29.8	26.0	21.0	68.2	62.0	54.2
2	20 ohm cm CG	90/60	425	30.6	28.5	26.0	69.5	66.3	60.3
3	20 ohm cm Monx	90/60	425	26.6	23.5	21.1	63.1	57.2	53.6
4	100 ohm cm FZ	90/60	425	26.0	23.3	21.6	63.1	58.0	54.7
5	20 ohm cm FZ	90/60	350	31.3	28.8	26.4	76.4	71.9	64.2
6	20 ohm cm CG	90/60	450	31.7	24.4	22.3	68.6	58.5	54.0
7	20 ohm cm Lopex	90/60	425	31.5	28.4	24.7	72.6	66.7	62.9
8	100 ohm cm FZ*	90/60	425	27.8	23.7	21.0	66.9	60.3	53.6
9	20 ohm cm FZ	90/60	425	29.0	27.1	25.2	67.1	62.9	59.8
10	20 ohm cm CG	90/60	425	32.0	29.0	26.0	70.5	65.0	59.6

*Special cell with phosphorus region at the junction

or above for 50% of the cells, which in most cases was higher than the top 5% of the short circuit currents in the other lots.

Figure 29 summarizes the maximum power distributions of all ten lots on one curve. Maximum power levels are shown for the 5, 50, and 95% points of the cells in each lot. The widest distribution spreads were obtained for Lot1 and Lot 6 which were crucible grown cells. This is not a problem inherent in crucible grown lithium cells since Lot 2, which was also crucible grown cells, had one of the narrowest distributions. In the case of Lot 1, it was the only lot in which the cells were boron diffused without using dummy cells. Dummy cells were used in the boron diffusions for Lot 2 cells and this, more than the starting resistivity, would seem to be the reason for the difference in distributions. The distributions remained relatively narrow until Lot 6. Lot 6 had a very wide distribution and this seemed to be caused by the differences in material discussed previously. Silicon from two different ingots was used and the cells from the second ingot had much higher outputs than the cells from the first ingot. The distributions for Lots 7 and 8 were narrower than for Lots 1 and 6, however, they were not as narrow as Lots 2 through 5. Lot 7 consisted of Lopex lithium cells and, as previously mentioned, had an unusually wide range in open circuit voltage which also resulted in a relatively wide maximum power range. The special cells fabricated for Lot 8 are quite different from the standard lithium cell in processing and output, so the relatively wide distribution is not too surprising. Lot 9, 20 ohm cm float zone lithium cells, had the narrowest distribution of all the lots. Lot 10 used the same diffusion and material parameters as Lot 2 and the minimum output for 95% of the cells was the same for both Lots -- 26.0 mW. However, higher outputs were obtained for the top 50% of the cells and this resulted in a 1.4 mW increase in the maximum power range.

The short circuit current distributions for all ten lots are summarized

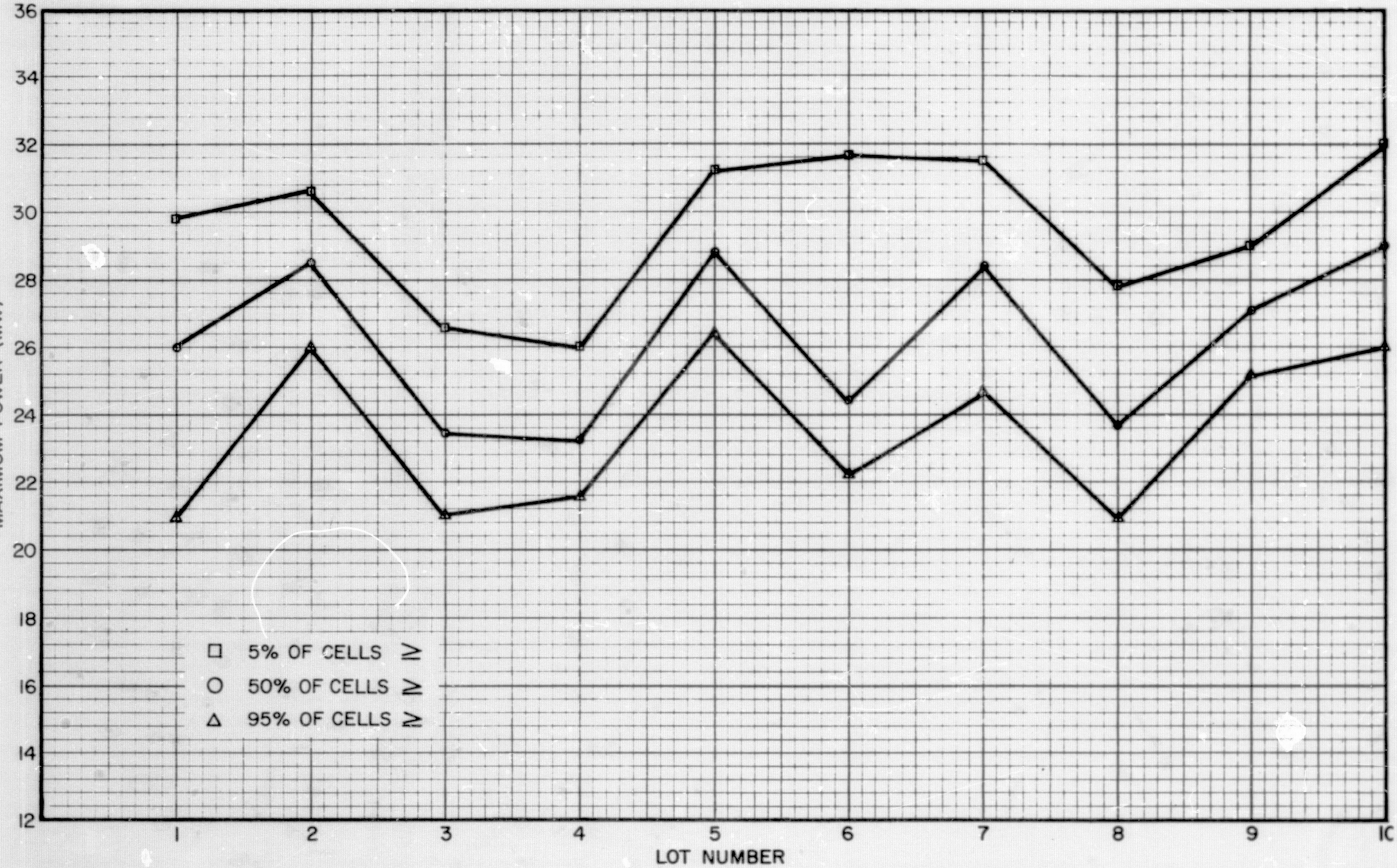


Figure 29. Summary of the Maximum Power Distributions of All Ten Lots.

in Figure 30 . The short circuit current varies 1.5 to 2 mA for each mW in maximum power and, with one exception, the short circuit current distributions resemble the maximum power distributions. The exception, Lot 5, had a wide short circuit current distribution; however, due to lower open circuit voltages for the cells which had very high short circuit currents, the maximum power did not vary as much as the short circuit current.

In general, the lithium cells fabricated from crucible grown silicon had the highest outputs. Whether or not these higher output cells will provide the best radiation resistance still remains to be determined since the radiation testing and analyses are being done by other laboratories. Improvements have been made in cell efficiencies for all cell designs during the past year. It is assumed that these improvements have been associated with process changes and control that have no effect on the radiation recovery process. The net result should be lithium doped solar cells that are capable of putting out more power after radiation exposure than was available with lithium cells made during the previous year.

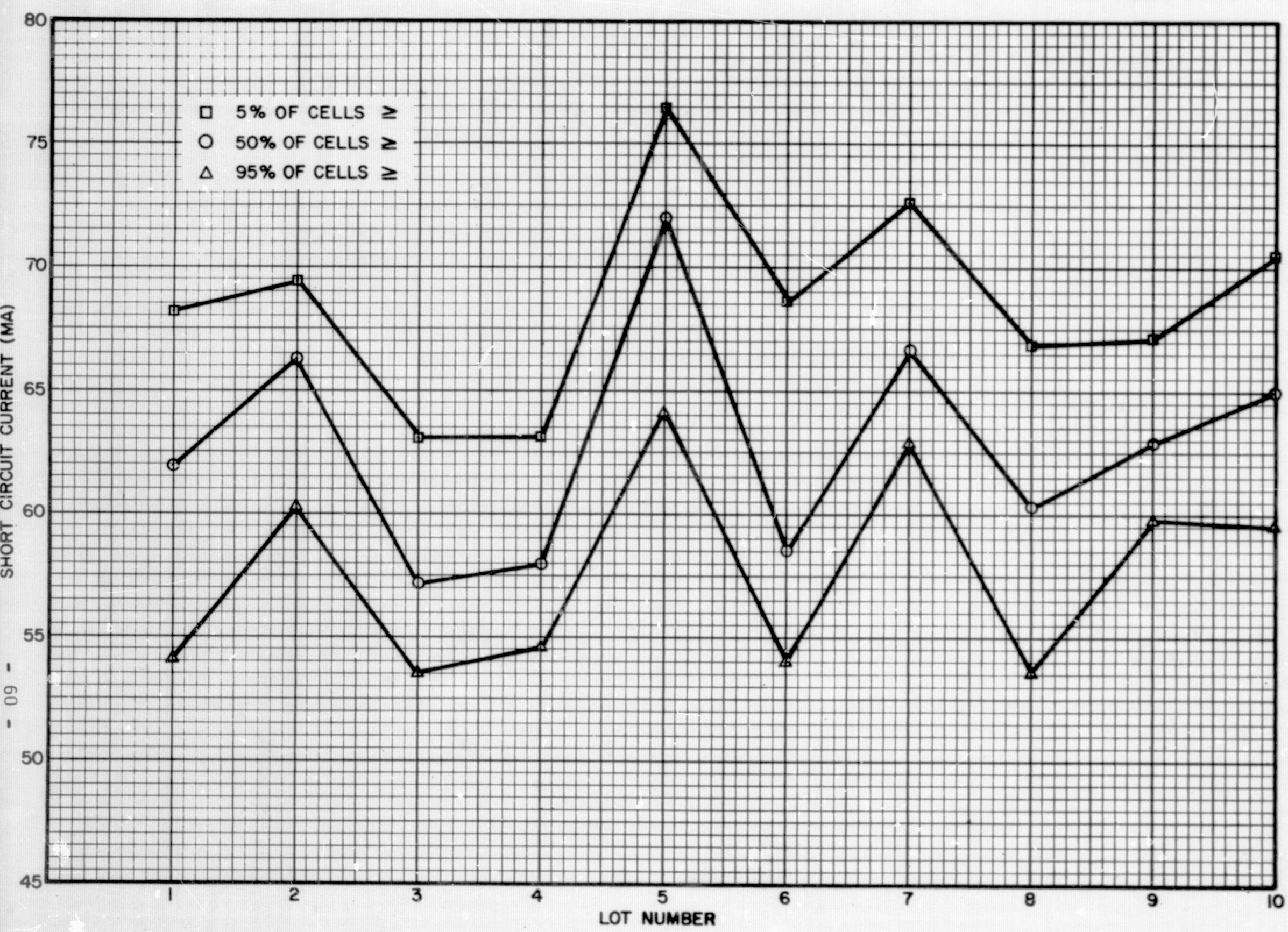


Figure 30. Summary of the Short Circuit Current Distributions of All Ten Lots.

3.0 CONCLUSIONS

It has been shown during this contract through the experimental work and the statistical analyses of the cells fabricated for shipment to JPL that the efficiency and uniformity of cell outputs was improved. It is believed that the significant factor which resulted in narrower distributions after Lot 1 was a result of a process change that involved the use of dummy slices on part of the boat during boron diffusion.

The SiO coating was shown to be superior as an antireflection layer to the natural blue layer obtained from boron diffusion. The SiO alone was also superior to a combination of the natural blue layer and SiO.

Sintering improved the output of crucible grown lithium cells in varying degrees. Some cells with low outputs showed particularly large improvements which may have indicated that stresses in the silicon crystal lattice were being relieved.

The fabrication of the various types of cells for each lot of sixty cells statistically demonstrated several things. Crucible grown lithium cells can be made with higher efficiencies than float zone lithium cells if the same lithium diffusion parameters are used. The efficiency of float zone lithium cells can be raised to a comparable level if the lithium concentration is reduced by the use of a lower diffusion temperature.

Lithium cells with efficiencies comparable to N/P cells have been made and, therefore, if these cells have good radiation damage recovery, they should be superior to N/P cells as radiation resistant solar cells.

4.0 RECOMMENDATIONS

The emphasis during this contract has been on improving the uniformity and output of lithium doped solar cells. Improvements can still be made, but at this point it has been demonstrated that lithium doped solar cells can be made with efficiencies of 10.0-11.0% AMO efficiencies. Crucible grown lithium cells have very high efficiencies and they are comparable to standard N/P cells. With this goal being reached, the emphasis should now be shifted to obtaining optimum recovery after radiation. Since any further improvements in cell output will probably be minor and only affect the radiation resistance in a minor way, other areas more important than process improvements should be investigated. Such parameters as dopants, oxygen levels, heat treatments, and N^+ regions may have significant effects upon the radiation resistance and they should be thoroughly investigated.

Some work should also be continued on improving cell outputs and developing more economical processes. This work should include, but not necessarily be limited to the following areas. Further investigations of lithium application by evaporation should be made since this technique would greatly reduce or eliminate any stresses which may presently occur during lithium diffusion.

Intensive work should be performed on the diborane diffusion source since the present BCl_3 source has its drawbacks with respect to the number of cells per diffusion, the etching action which is undesirable for the N^+ special design cell, and the stresses generated which will beome a more significant problem as the emphasis shifts to larger area cells.

The sintering investigation should be expanded to determine whether sintering is beneficial for all types of lithium cells. The effect of sintering should also be analyzed with respect to effects upon radiation recovery characteristics.

5.0 NEW TECHNOLOGY

None.