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Manufacturer of Space Age Solid State Devices

Development of Lithium Diffused Radiation Resistant Solar Cells

Report No. 3

First Quarterly Report

By: P. Payne

15 July 1968

JPL Contract No. JPL 952247

Heliotek, a Textron Company

12500 Gladstone Avenue

Sylmar, California

heliotek

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ABSTRACT

During this quarter, various parameters of the lithium diffusion were investigated with respect to uniformity of the cell electrical characteristics. A new lithium furnace was set up. Lithium diffusions were done in an helium atmosphere and compared to those done in a nitrogen atmosphere. Cell position on the diffusion boat during lithium diffusion was investigated with respect to cell electrical characteristics. Study of the effect of boron diffusion process parameters on lithium cell electrical characteristics was also started.

Two shipments of sixty cells each have been fabricated and the first has been submitted to JPL for radiation testing. Yield analyses has started and will be done for each shipment of cells. This analysis is expected to be a valuable tool in analyzing progress with respect to process control and in selecting optimum parameters.

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1.0 INTRODUCTION

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

With respect to starting material, the type of crystal is of particular interest. The room temperature or low temperature recovery of lithium cells fabricated from crucible grown silicon has been a recent enough discovery that very little information has been obtained on these cells. The extremely good characteristics of these cells make 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 lower efficiencies than standard 10 ohm cm N/P cells. Even so, the lithium cells compare favorably after radiation to the N/P cells. It is 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 have been obtained, the problem is one of improving uniformity and yields by improving processes and techniques. The main areas of study for improving cell efficiency will be the lithium and boron diffusions.

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

2.0 TECHNICAL DISCUSSION

2.1 DIFFUSION STUDIES

A multi-zoned lithium diffusion furnace was set up and checked out during this period. This furnace has a uniform heat zone of eight inches. Previously only a small single-zoned furnace had been used for lithium diffusions and this was inadequate because there was no uniform temperature zone. Both nitrogen and helium gas lines were installed in the new furnace system. Nitrogen has been used exclusively in the past for lithium diffusions, however, it is known to react with lithium. Therefore, a series of experiments were run where helium was investigated as an ambient to determine whether or not it would be an improvement in the cell process. The short circuit current and maximum power distributions of cells diffused in helium and nitrogen are shown and can be compared in Figures 1 and 2. The short circuit currents of cells diffused in helium were 2 to 5 mA lower than those diffused in nitrogen; however, this was not as serious as the difference in maximum power and open circuit voltage. Figure 2 shows that the maximum power of cells diffused in an helium atmosphere was 2 to 4 mW lower than the cells diffused in nitrogen. The material used in all of the runs above was 1 ohm cm crucible grown silicon slices. This material typically produces a very good I-V characteristic curve with a very sharp knee. The major part of the maximum power loss for the cells diffused in helium was a rounding of the knee. This pronounced difference in the I-V characteristics is believed to be attributed directly to the ambient used during lithium diffusion. There is a possibility that the results were biased by problems related to boron diffusions, since several different boron diffusion lots were used. This is unlikely though, since in one experimental run lithium diffusions were done in both nitrogen and helium atmospheres utilizing cells from the same boron diffusion lot. In this run the results were the same as observed in the other runs in which the cells diffused in helium were inferior to those diffused in nitrogen. An explanation of this phenomenon has not been postulated, however, more work will be done to evaluate the effect of carrier gas on cell performance and particular care will be taken to split boron diffusion lots and maintain similar processing such that prior to the lithium diffusions the cells to be diffused in nitrogen will be identical to those to be diffused in helium.

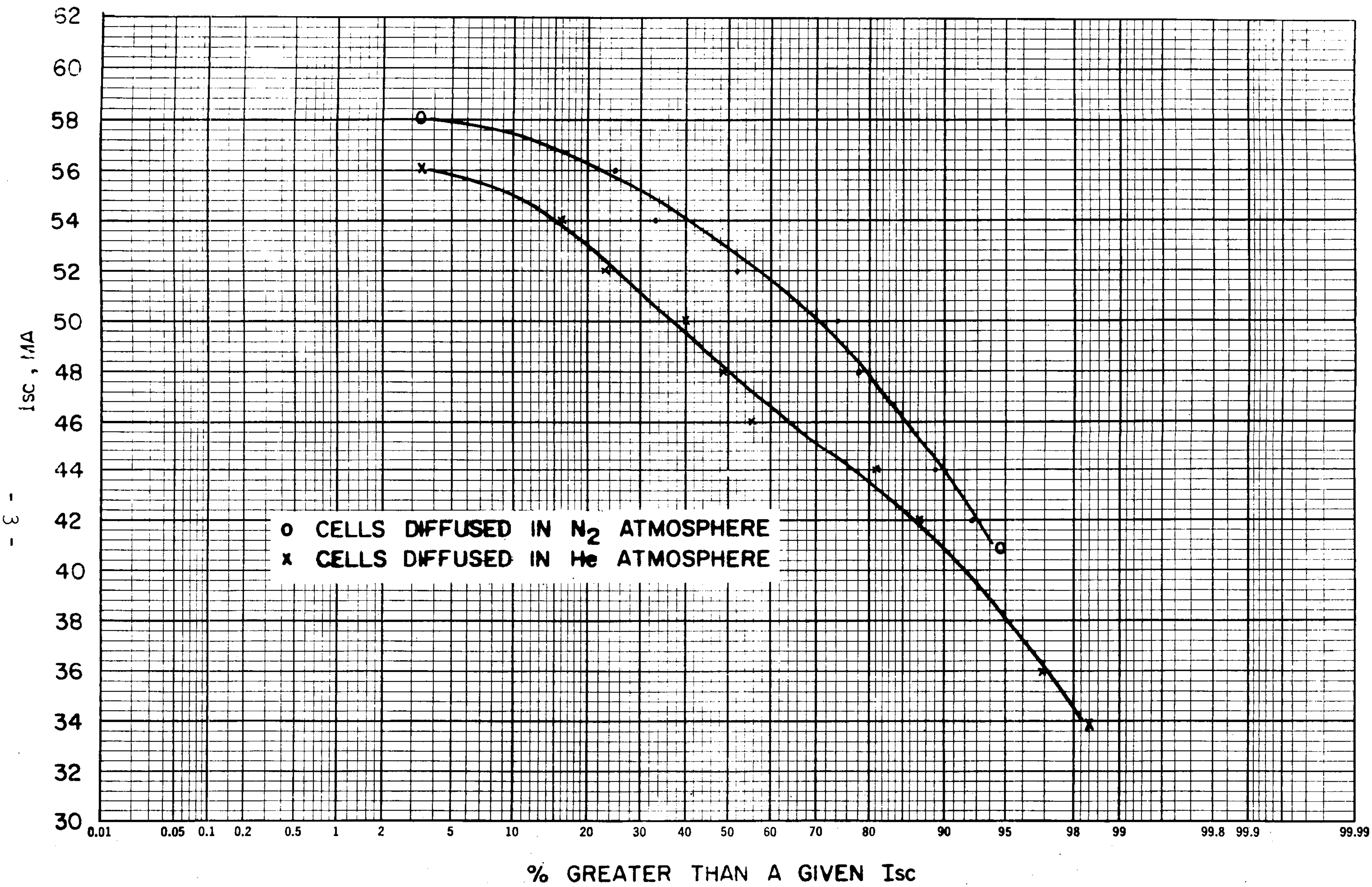

Fig. 1. Short Circuit Current Distribution of Lithium Cells Fabricated from 1 ohm cm Czochralski Grown Silicon. 27 Cells diffused in N_2, 31 cells diffused in He. Measured in 100 mW/cm^2 tungsten light source.

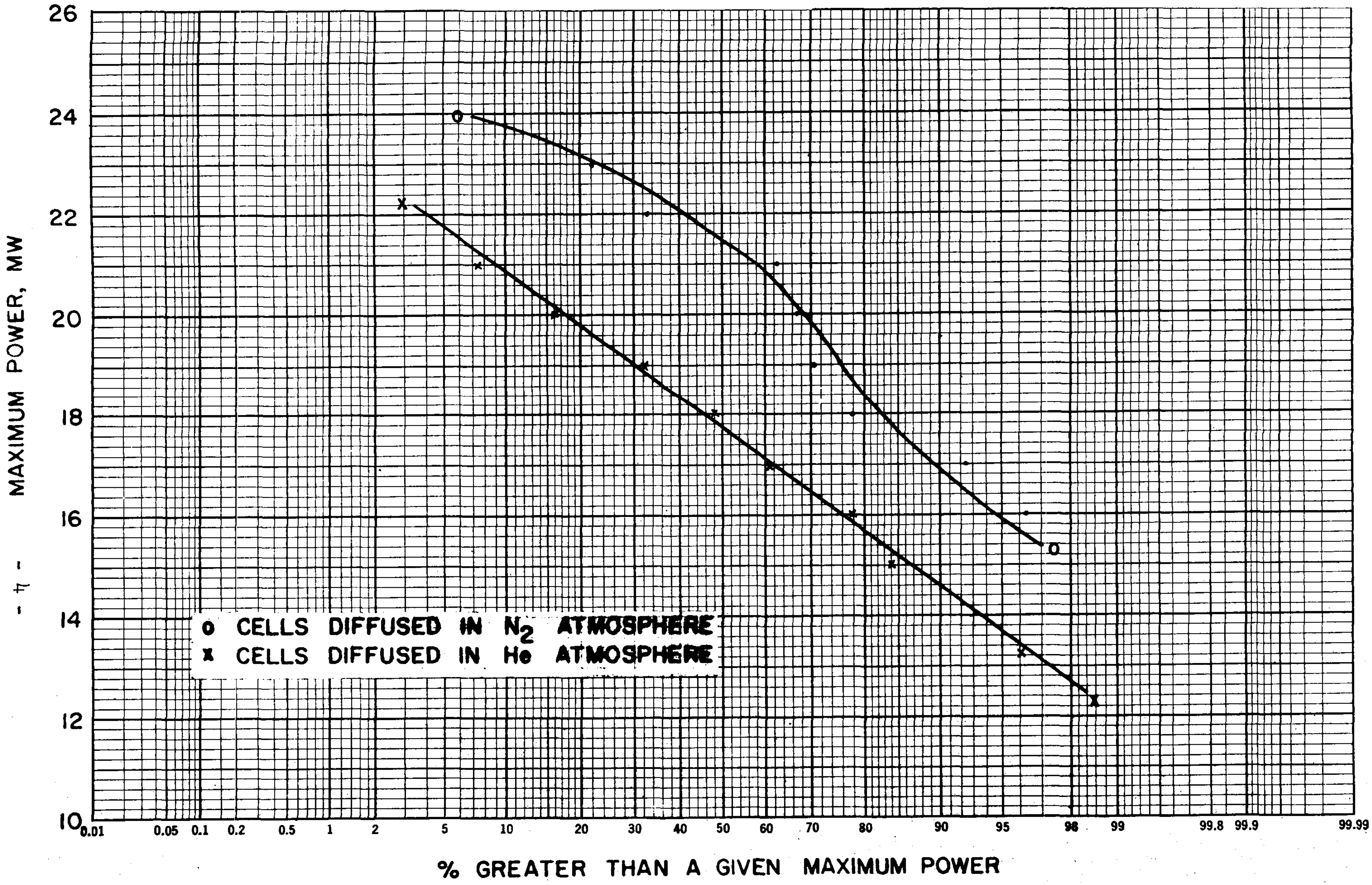

Fig. 2. Maximum Power Distribution of Lithium Cells Fabricated from 1 ohm cm Czochralski Grown Silicon. 27 cells diffused in N_2, 31 cells diffused in He. Measured in 100 mW/cm^2 tungsten light source.

Large variations in electrical characteristics of lithium cells is one of the biggest problems at this time. In general these variations are present in every lithium diffusion lot. For this reason it was decided to investigate lithium diffusion variables with respect to uniformity of electrical characteristics. Past experience has shown that the amount of lithium applied to the cell surface has a significant effect. With thick layers of lithium there is a high probability that large metallic spheres of lithium are formed which are highly detrimental. These large spheres are not caused by large chunks of lithium in the oil paste source because the lithium is strained through a fine screen prior to use. Instead they begin to form as the oil evaporates and the lithium begins to melt in the diffusion furnace. With thick layers they continue to grow as the lithium melts. Their physical effect upon the cell, however, is the same as oversized grains of lithium. Large alloy pits are formed in the silicon and in many cases a stress is formed which is sufficient to break the cell. Those cells which don't break are most probably seriously damaged and this could account for a low output. Application of moderately thin lithium layers results in fewer of these large spheres forming. Also, the ones that do form later in the diffusion process create smaller pits. It has been determined that if the lithium layer is kept thin enough these large spheres do not form. This sphere formation and pitting has been essentially eliminated which has reduced the number of broken cells, but there still is a significant variation in the uniformity of the electrical characteristics.

Two other aspects of the lithium diffusion which could affect uniformity significantly could be the cleanliness of the parts and the cell position on the boat during diffusion. With respect to cell position during lithium diffusion, the oil vapors coming off the row of 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. 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 a contaminant. To check this, three diffusions were made, where after each diffusion and redistribution the tube was changed. The average short circuit current for this group of cells was 39 mA with a range from 35 to 43 mA. The same diffusion time and temperature normally give short circuit ranges anywhere from 40 to 50 mA. In another experiment two dummy diffusions were made after a clean tube was installed. Then a normal lithium diffusion run was made. In this case cells were obtained with the 40 to 50 mA short circuit current. Apparently, this collection of oil on the tube does not affect the diffusion and there appears to be a break-in period required for clean tubes. After approximately fifteen diffusions, the output again decreases, indicating there is a contamination build-up in the tube over many diffusion runs.

An investigation of the influence of the boron diffusion on the uniformity of the electrical characteristics of lithium cells was begun. By fabricating P/N cells without lithium it has been determined that cell position during boron diffusion affects the electrical output. During boron diffusion silicon is etched away from the slices by the BCl_3 gas. The amount of etching varies, but those cells which are first exposed to the gas flow are etched more than the cells further back on the diffusion boat. The cells which are etched the most have lower outputs than those with the least amount of etching.

To reduce the variations in electrical output caused by the etch rate variations, experimental boron diffusions were made using dummy slices on the front half of the boat. The cells from these boron diffusions showed a tighter range in the electrical characteristics than normal diffusions. The next section gives more detail on the actual output distribution observed with this type boron diffusion technique.

2.2 CELLS FOR SHIPMENT

The first shipment of cells was made from > 100 ohm crucible grown silicon which was lithium diffused ninety minutes and redistributed sixty minutes at 425°C. The same diffusion parameters were used for the second shipment, however, 20 ohm cm crucible grown silicon was used as the starting material.

In fabricating the required sixty cells for each shipment lot, 120 cells for the first group and 113 cells for the second group were diffused and processed. This resulted in a group large enough for good selection and also provided a large number of cells for statistical analysis. This statistical analysis was made on all cells, rather than just the sixty cells selected for shipment to JPL, and is expected to be valuable in indicating progress with respect to uniformity and increased efficiency throughout the contract period. Figures 3 through 6 show short circuit current and maximum power distribution curves of all the cells processed for the first two shipment lots.

The cells for the first shipment showed a rather wide short circuit current distribution which is shown in Figure 3. The mean I_{sc} was 62 mA and 95 percent of the cells had short circuit currents above 54.2 mA while 5 percent were above 68.2 mA. Figure 4 shows two short circuit current distribution curves of cells fabricated for the second shipment lot. The lower curve includes all the cells fabricated while the higher curve has five diffusion runs eliminated. These five diffusion runs were consecutive and the average cell output for all five runs was significantly lower

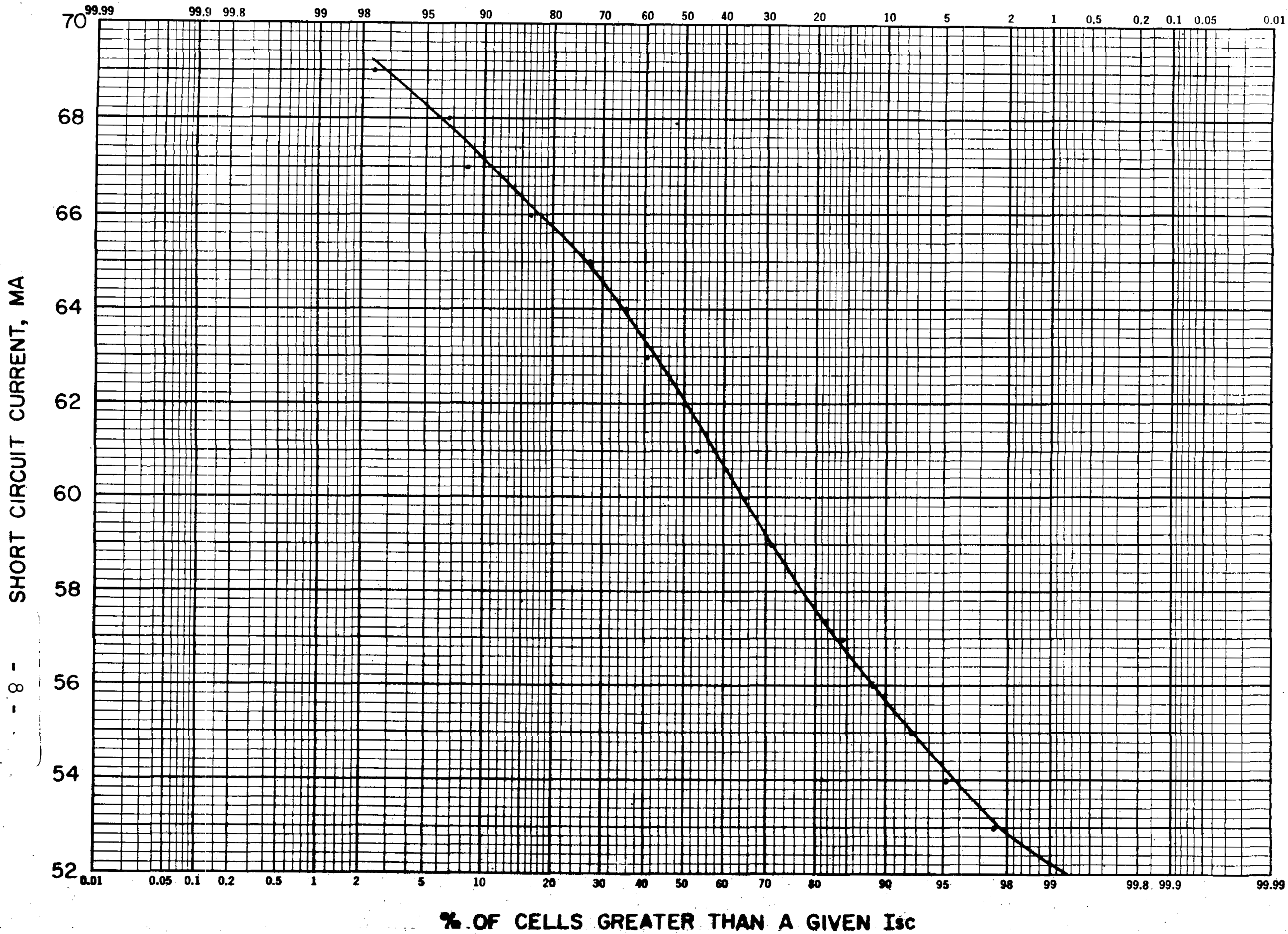

Fig. 3. Short Circuit Current Distribution of Lithium Cells Fabricated for the First Shipment Lot. >100 ohm cm Czochralski Grown silicon, diffused 90 minutes, redistributed 60 minutes at 425°C. 120 cells measured in solar simulator at 140 mW/cm .

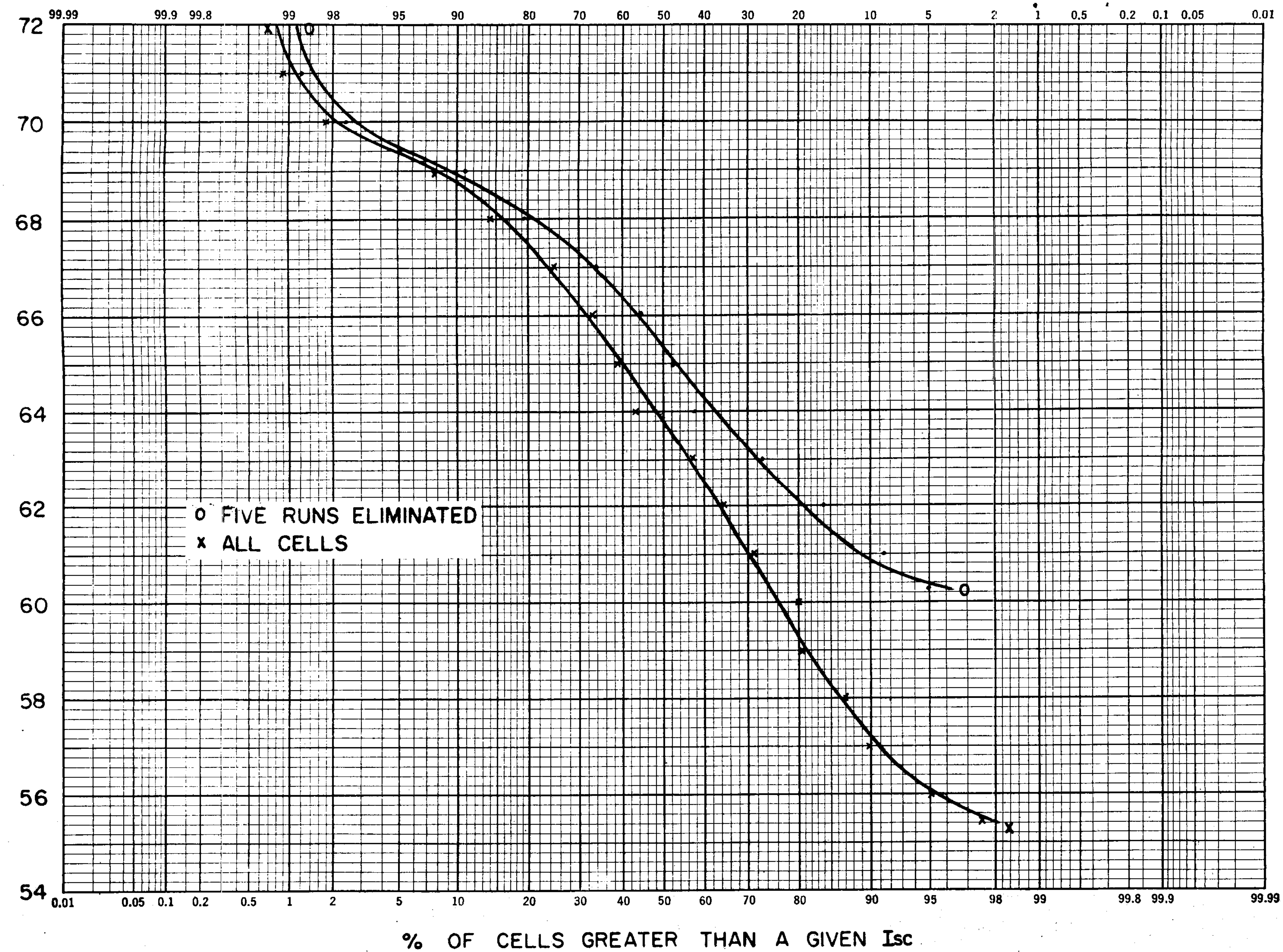

Fig. 4. Short Circuit Current Distribution of Lithium Cells Fabricated for the Second Shipment Lot. 20 ohm cm Czochralski Grown silicon, diffused 90 minutes, redistributed 60 minutes at 425°C. "0"= 81 cells, x = 113 cells. Measured in solar simulator at 140 mW/cm^2.

than the cells from other runs. The cause of this lower output could not be traced, however, the fact that they were consecutive and unusual would seem to indicate that some uncommon variable went out of control for 1 to 2 days. Both distributions show an improvement over the first shipment distribution. Considering only the lower curve, the mean short circuit current increased 1.7 mA to 63.7 mA. Five percent of the cells were above 69.4 mA (1.2 mA improvement) and 95 percent of the cells were above 56 mA (1.8 mA higher than the first shipment). It is at the 95 percent point that the effect of the five low output runs is particularly significant. Eliminating the five unusual runs, 95 percent of the cells are above 60.4 mA compared to the 56 mA value for all cells!

Maximum power for the two shipment lots is shown in Figures 5 and 6. The mean increased from 26.1 mW for the first lot to 27.9 mW for the second lot. Of the cells in the first lot, 95 percent were above 22 mW, while in the second lot, 95 percent were above 22.9 mW. If the five runs were eliminated, the second lot would have had 95 percent of the cells above 26.0 mW.

The only differences between lots 1 and 2, besides the time period of fabrication, were the starting material and the boron diffusions. Both materials were doped to the same level with lithium. It would appear that the starting material resistivity would not account for the improvement in the final output, however, it is a possibility. The boron diffusions for the second lot used dummy cells in an attempt to reduce the etch rate and electrical output variations. This would seem to be the primary variable affecting output and improving the distribution of the second lot of cells.

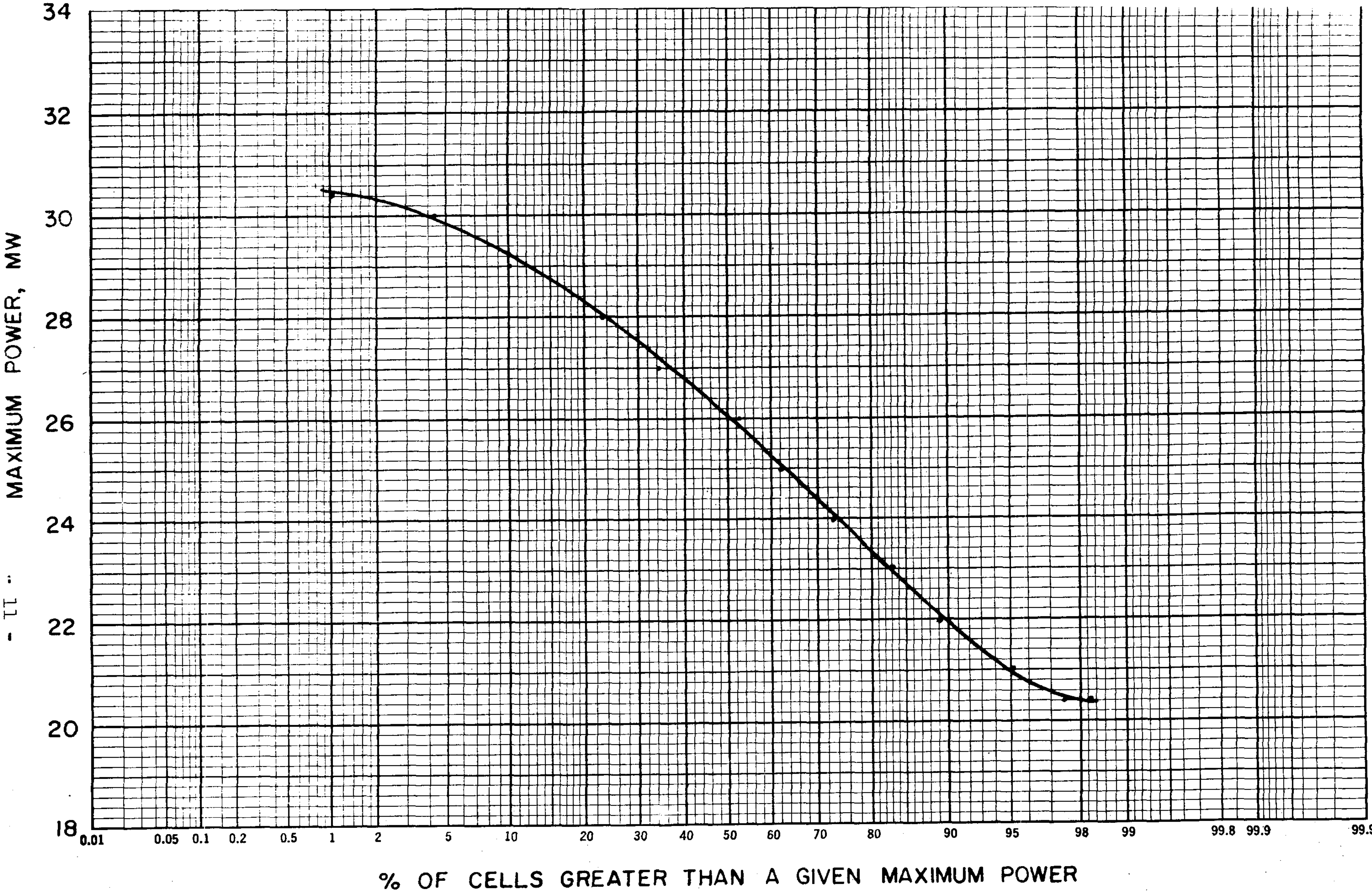

Fig. 5. Maximum Power Distribution of Lithium Cells Fabricated for the First Shipment Lot. >100 ohm cm Czochralski Grown silicon, diffused 90 minutes, redistributed 60 minutes at 425°C. 120 cells measured in solar simulator at 140 mW/cm^2.

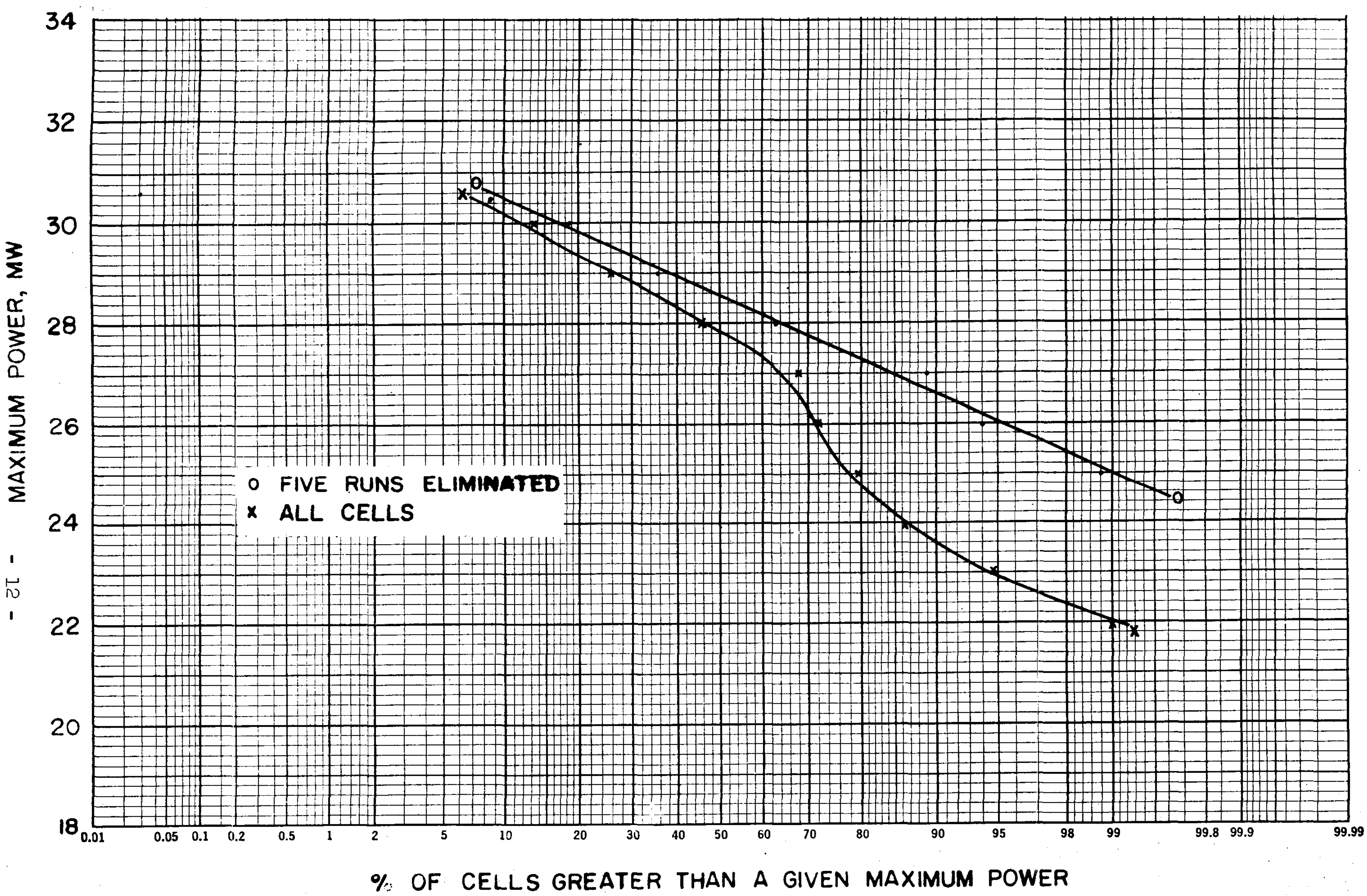

Fig. 6. Maximum Power Distribution of Lithium Cells Fabricated for the Second Shipment Lot. 20 ohm cm Czochralski Grown silicon, diffused 90 minutes, redistributed 60 minutes at 425°C. "O" = 81 cells, x = 113 cells. Measured in solar simulator at 140 mW/cm^2.

3.0 CONCLUSIONS

The refinements made in the lithium diffusion process so far have eliminated only gross problems. The application of a thin layer of lithium has reduced breakage; the use of several lithium dummy runs after changing the diffusion tube has eliminated the lower efficiency cells obtained from the first couple of diffusions in a clean tube. An attempt to correlate cell output to cell position on the diffusion boat during lithium diffusion gave negative results. The cell output variations are significant enough to warrant much more investigation, both of the lithium and the boron diffusions. Any improvements made in the lithium diffusion process will be limited by all the problems encountered in the boron diffusion. If uniformity is a problem in the boron diffusion, then improvement of uniformity of lithium diffusions is only half the solution. The use of dummy cells on part of the boat during boron diffusion appears to have improved the efficiency and uniformity of the cells, however, more work must be done to substantiate this improvement.

Higher efficiency lithium cells were obtained using crucible grown silicon as starting material as compared to float zone silicon. In general, higher open circuit voltages could be obtained from lithium cells fabricated from crucible grown silicon.

The average output of the cells fabricated for the first shipment lot was 26 mW or an AMO efficiency of 9.6 percent, and for the second shipment the average output increased to 28 mW or an AMO efficiency of 10.3 percent.

4.0 RECOMMENDATIONS

The lithium diffusion should be studied more extensively; the effect of different methods of source application should be investigated.

The apparent improvement in uniformity of cell output obtained by using dummy slices in boron diffusions should be confirmed.

New sources for boron diffusion should also be studied since the use of dummy cells to improve uniformity limits even more the small number of cells which can be done in a boron diffusion.

5.0 NEW TECHNOLOGY

None.