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LITHIUM-DOPED SOLAR CELLS FOR SPACE USE

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I. INTRODUCTION

This paper summarizes the lithium-doped solar cell research and development carried out by Heliotek over the past nine months under JPL Contract 952547, Part II. The work performed can be separated into two basic areas: (1) experimental work aimed at the improvement of cell processes and efficiencies, and (2) demonstration of these improvements by the fabrication and statistical analyses of quantities of various lithium-doped solar cell types.

Over the past several years the lithium-doped solar cell has progressed from a laboratory curiosity, because of its unusual radiation damage recovery characteristics, to a high-efficiency radiation-resistant solar cell. Although significant improvements are still being made and a better understanding of the device has been achieved, it is a good time to stop and evaluate the state-of-the-art. Some important factors are:

(1) Lithium-doped solar cells have been made that have exhibited higher power outputs than conventional N/P solar cells after irradiation to a fluence of $>10^{15}$ 1-MeV electrons per cm^2.

(2) Lithium-doped cells have recently been made with very high efficiencies that are substantially higher than N/P cells.

(3) The size of lithium-doped cells have been increased from 1 × 2 cm to 2 × 2 cm and even 2 × 6 cm as the result of the elimination of the boron diffusion stresses.

These factors indicate that the lithium-doped solar cell basically meets or exceeds the electrical and radiation resistance characteristics of conventional N/P solar cells and improvements with lithium cells are still being made. The logical step to be made next is the pilot production of these cells, so that questions of cost, reproducibility, reliability, and space worthiness can be answered.

This paper summarizes the work that has been done in the past nine months in respect to lithium cell power output, cell thickness, large area cells, integrity of cell contacts and types of experimental cells prepared for radiation tests.

II. SUMMARY OF PREVIOUS DEVELOPMENT EFFORTS

The lithium-doped P/N solar cell has gone through distinct development stages over the past four years, with each stage showing a definite improvement in initial and post-irradiation recovered efficiencies.

During the initial work (1966 to 1967) float-zone silicon was used. Lithium diffusion times ranged from 5 to 120 min, and diffusion temperatures ranged from 350 to 500°C. The concentration gradients in the silicon slice were very steep, causing lithium cell instability, as exhibited by shelf-life degradation and redegradation after post-irradiation recovery. In order to reduce this gradient, redistribution cycles (removal of the excess lithium from the cell surface and further heating of the cell to move the lithium deeper into the slice) ranging from 30 to 120 min were used. Redistribution cycles produced higher output cells

with little change in the recovery characteristics. Table 1 shows typical air mass zero (AMO) electrical output values for cells diffused 5 and 90 min and the change in output after 60- and 120-min redistributions.

Discovery in 1967 of the recovery capabilities of lithium-doped solar cells fabricated from crucible grown (C. G.) silicon led to extensive investigation in this area. The higher oxygen concentration C. G. lithium cells exhibited retarded room temperature post-irradiation recovery; however, recovery rates equivalent to those obtained with low oxygen concentration lithium cells were observed when the cell temperature was raised to 60 or 100°C. Cell stability, both shelf-life and after radiation recovery, which was poor for some float-zone lithium cells, was not a problem with C. G. lithium-doped solar cells. In June 1969 the output of C. G. lithium cells was typically about 2 mW higher (28. 3 versus 26. 5 mW) than similarly doped float-zone lithium cells.

The next stage of development was the investigation of lower lithium diffusion temperatures. Eight-hour diffusions at 325°C were performed and typical C. G. lithium cell efficiencies were approximately 2 mW higher (30. 0 versus 28. 3 mW) than C. G. lithium cells that were diffused 90 min and redistributed 60 min at 425°C. The outputs of these cells after being irradiated with 1-MeV electrons to a level of 3×10^{15} e/cm^2 were 11 to 20% higher than the 19. 5 mW average output of 10 Ω-cm N/P cells.

These improvements in lithium cell characteristics were made independently of other processes in the fabrication procedure. They were primarily due to changes in lithium diffusion parameters. In order to further improve cell output, develop procedures which could be used in production and show capability of meeting basic requirements for space quality cells, investigation in areas such as the boron diffusion, method of lithium application, and contact quality has been done.

III. BORON DIFFUSION INVESTIGATION

The objective of the boron diffusion investigation has been to develop a boron diffusion process which could be used to diffuse large quantities (≥100 blanks per diffusion) of stress-free high-efficiency cells. BCl_3 has been the diffusion source most commonly used in fabricating lithium-doped solar cells. This diffusion source was optimized for fabrication of P/N cells (432-μm thick 1 × 2 cm C. G. silicon blanks) early in the 1960's. This process had a very serious limitation in that it could not be used for fabricating thin cells or cells of a 2 × 2 cm size or larger without a significant amount of bowing due to stresses introduced during the diffusion. Therefore, two methods for reducing the stresses generated during boron diffusion were investigated: (1) a modification of the standard BCl_3 diffusion, involving reduction of the boron deposition time, and (2) use of BCl_3 with O_2.

The BCl_3 diffusion, as it had been used over the years, consisted of an 8-min warmup time, an 8-min boron deposition time and a 10-min diffusion time. During the boron deposition the BCl_3 reacts with the silicon; the silicon is etched and a heavy deposit of boron silicides (Ref. 1) is left on the cell surface. This etch reaction and buildup of boron silicides had previously been shown to be influenced by cell position on the boat during diffusion, with the cells first exposed to the BCl_3 flow showing the greatest amount of silicon etched, the highest frequency of bowing, and the lowest output. In an experiment to determine whether the stresses could be reduced by reduction of the boron deposition time, the boron deposition time was varied from 8 min down to 2 min. Both lapped and etched blanks were included in the experiment. It was found that the etched blanks (350 μm thick) were more susceptible to bowing than the lapped blanks (also 350 μm thick), i. e., etched cells (1 × 2 cm, 350 μm thick) were bowed after using an 8-min boron deposition time, whereas lapped cells were not. Reduction of the boron deposition time to 2 to 5 min reduced this heavy boron layer and produced unbowed cells. By using a 2-min boron deposition time 150 μm thick 2 × 6 cm blanks were then successfully diffused with no bowing. Typically, 8-min diffusions have produced bowed 2 × 2 and 2 × 6 cm cells (250 μm thick) with the radius of curvature being as small as 8. 5 cm. The absence of bowing of the large area cells achieved with a 2-min boron deposition time indicated that the stresses were reduced considerably.

The other process modification investigated for reduced stresses was BCl_3 with O_2. Just as with the previously described diffusion, an 8-min warmup time was used. The O_2 was introduced into the BCl_3 gas just before the gas flow entered the diffusion tube. The BCl_3 reacted with the O_2 to produce B_2O_3, which deposited on the cells as a glass layer. This glass layer and the subsequent diffusion did not bow the cells.

Since low-stress cells were produced with both processes discussed above, the two processes were compared to determine which resulted in the best cell electrical output. Two groups of 100 cells were fabricated using the two different processes. The silicon blanks used were 300 to 380 μm thick with a resistivity of 0. 2 to 1. 2 Ω-cm. These were P/N cells with no lithium present. Etched rather than lapped blanks were used since, unlike the standard BCl_3 diffusion, neither of these diffusion processes etch sufficient silicon to remove the crystal surface damage present on a lapped blank. As shown in Fig. 1, the AMO output of cells diffused in BCl_3 (no O_2) with a 2-min deposition time, averages 3 to 4 mW higher than the output of the cells diffused in BCl_3 with O_2. The lower output of the cells diffused with O_2 was primarily due to lower open-circuit voltage and higher series resistance. The average open-circuit voltage of the cells diffused with O_2 was 590 mV, whereas the open-circuit voltage of cells diffused without O_2 was 615 mV. The series resistance of cells from each group was measured. The series resistance of the cells diffused with O_2 was typically around 0. 8 Ω, whereas for the cells diffused with no O_2 the series resistance was around 0. 3 Ω. Table 2 summarizes the electrical data on these two groups of cells.

At the present time, although neither of these two diffusions discussed can be used for diffusion of one hundred cells or more per diffusion, the BCl_3 diffusion with a short deposition time and without O_2 produces the best combination of low stress and high efficiency.

IV. EFFECT OF BORON DIFFUSION PARAMETERS ON IMPROVEMENTS IN LITHIUM CELL OUTPUT

Once reduced stresses were obtained on P/N cells by reducing the boron deposition time, the effects of this process change on lithium cell output were investigated. Experimental lithium diffusions were performed using 20 Ω-cm Lopex silicon material with both 2- and 8-min boron deposition times. Both groups were placed in the same lithium diffusion. The electrical characteristics of these cells are summarized in Table 3. The short-circuit current of the lithium cells subjected to the 2-min boron deposition averaged 11 mA higher when measured in a 100 mW/cm^2 tungsten light source and 6 mA higher when measured in a solar simulator (AMO) than lithium cells subjected to an 8-min boron deposition time. Figures 2 and 3 show the short-circuit current distribution obtained in the two light sources for the two groups of cells (20 cells per group). These distributions show that the 2-min boron deposition results not only in higher, but more uniform, short-circuit currents.

In addition to the higher short-circuit currents obtained for lithium cells subjected to a 2-min boron diffusion, open-circuit voltages (measured at 25°C) as high as 615 mV were obtained; the highest open-circuit voltage observed for cells diffused with an 8-min boron deposition was 595 mV. The higher short-circuit currents and open-circuit voltages led to Lopex lithium cell AMO outputs ranging from 27.6 to 31.7 mW, rather than 23.6 to 28.8 mW as was obtained when an 8-min boron deposition was used.

Sintering of the contacted cell was investigated to determine its effect upon the curve factor, which for some cells was below 0.70. Sintering consisted of a heat treatment at 605°C for 6 min in an H_2 atmosphere. In most cases the sintering improved the curve factor slightly; in addition the AMO short-circuit current of lithium cells subjected to a 2-min boron deposition time increased 3 to 5 mA with sintering. Typically improvements of 10 to 25 mV in open-circuit voltage were also observed. These improvements in curve factor, open-circuit voltage, and short-circuit current resulted in AMO outputs 1 to 4 mW higher than the unsintered cell output. Figure 4 shows I-V curves of a typical cell before and after sintering. The open-circuit voltage increased by 25 mW (600 to 625 mV); the short-circuit current increased by 3 mA (71.5 to 74.5 mA); the curve factor increased from 0.706 to 0.721; and the output increased by 3.3 mW (30.3 to 33.6 mW).

In fabricating Lopex lithium cells for Lot 11 the following lithium diffusion schedules were used: (1) 3 h at 340°C, (2) 7 h at 340°C, (3) 3 h at 360°C, and (4) 7 h at 360°C. Figure 5 shows the distributions in maximum power (after sintering) for the different groups of Lopex lithium cells. The various lithium diffusion parameters produced similar AMO outputs with the outputs for all the groups ranging from 29 to 34 mW. This is equivalent to an AMO efficiency range of 10.9 to 12.8%. The median efficiency is 11.9%. These efficiencies are the highest obtained on lithium cells thus far and are comparable to high-quality conventional N/P cells.

In Fig. 6 the Lopex cells which make up each group in Fig. 5 are treated as a single group and the AMO output is compared to a typical AMO output distribution of conventional 10 Ω-cm N/P cells. The lithium cell output is 3 to 10% higher than the N/P cell output. Even if, for some reason, the sintering step is eliminated from the process, the lithium cell outputs are in the same range as the 10 Ω-cm N/P cells. Figure 7 compares I-V characteristic curves of a typical 10 Ω-cm N/P cell, and a typical lithium cell from this group of 105 lithium cells. These curves show that the high lithium-doped cell output is due to short-circuit currents as high as 10 Ω-cm N/P cell currents and higher open-circuit voltages.

Not only has the BCl_3 diffusion with a 2-min boron deposition resulted in improved lithium cell output, but it has also made it possible to fabricate 2 × 2 and 2 × 6 cm lithium cells. Figure 8 shows various sized lithium cells which have been fabricated. Sample cells, 2 × 2 cm and 2 × 6 cm, which were fabricated from 20 Ω-cm crucible grown silicon and lithium diffused 8 h at 325°C exhibited efficiencies ranging from 10.3 to 11.3%.

V. CONTACT QUALITY

In order to evaluate Ti-Ag contact integrity, lithium-doped P/N cells were subjected to humidity and peel testing.

The humidity test consisted of exposing lithium cells with soldered contacts to 30 days of 90% relative humidity at 45°C. The cells were measured at 25°C in 100 mW/cm^2 tungsten light source before and after thirty days of humidity exposure. The cells exhibited 2.5 to 3.5% short-circuit current degradation, 0 to 2% current degradation at 450 mV, and no open-circuit voltage degradation. Peel tests were performed on these same cells after humidity exposure. The test consisted of soldering wires to both front and back contacts and pulling at a 90-deg angle to the cell surface until contact failure. The ten samples all exhibited peel strengths of 500 to 1000 g for both front and back contacts.

A tape peel test is also used to test contact integrity on unsoldered cells. Scotch brand adhesive no. 810 is applied to both front and back surfaces of the cells. If the contacts are weak, they will peel off with the tape. This test is used on all lithium cells fabricated and the failure level is less than 5%.

VI. CONCLUSIONS

Lithium-doped P/N solar cells meet the basic requirements of solar cells for space use. The efficiencies of the Lopex lithium cells which range from 10.5 to 12.8% are equal to or better than C.G. lithium cell and 10 Ω-cm N/P cell efficiencies. Reduction in the stresses introduced during boron diffusion has eliminated cell size restrictions and both 2 × 2 and 2 × 6 cm lithium-doped cells have been fabricated. The Ti-Ag contacts which are tested 100% with a tape peel test, and pull tested and humidity tested on a sample basis are comparable to the Ti-Ag contacts on N/P cells.

ACKNOWLEDGEMENT

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References

1. Powell, C. F., Campbell, I. E., and Gonser, B. W., Vapor Plating, p. 107. John Wiley & Sons, New York, 1955.

Table 1. Output of lithium-doped P/N solar cells

Diffusion temperature, °C	Diffusion time, min	Redistribution time, min	P_{max}, mW
425	5	–	25.8 to 27.3
425	5	60	29.2 to 29.4
425	5	120	30.4 to 30.6
425	90	–	25.5 to 27.0
425	90	60	26.7 to 27.6
425	90	120	28.3 to 29.3

Table 2. Electrical characteristics of 1 Ω-cm P/N cells (no lithium)

Description	BCl_3 (no O_2) 2-min deposition range (median)	BCl_3 (with O_2) range (median)
AMO output, mW	28 to 33 (30.5)	25 to 28 (26.9)
V_{oc}, mV	600 to 625 (615)	570 to 600 (590)
Series resistance, Ω	0.2 to 0.5 (0.3)	0.4 to 1.0 (0.8)

Table 3. Electrical characteristics of lithium-doped P/N cells 2-min versus 8-min boron deposition (20 cells per group)

Parameter	Boron deposition range (median)	
	2 min	8 min
I_{sc}, mA[a]	63.5 to 66.0 (65.0)	48.0 to 59.0 (51.0)
I_{sc} (AMO), mA	69.0 to 71.0 (70.4)	60.0 to 66.0 (63.7)
$(V_{oc})^b$, mV	571 to 612 (595)	552 to 595 (578)
Output (AMO), mW	27.6 to 31.7 (29.5)	23.6 to 28.8 (26.5)

[a]Measured in a tungsten light source at an intensity of 100 mW/cm^2.

[b]Measured at 25°C.

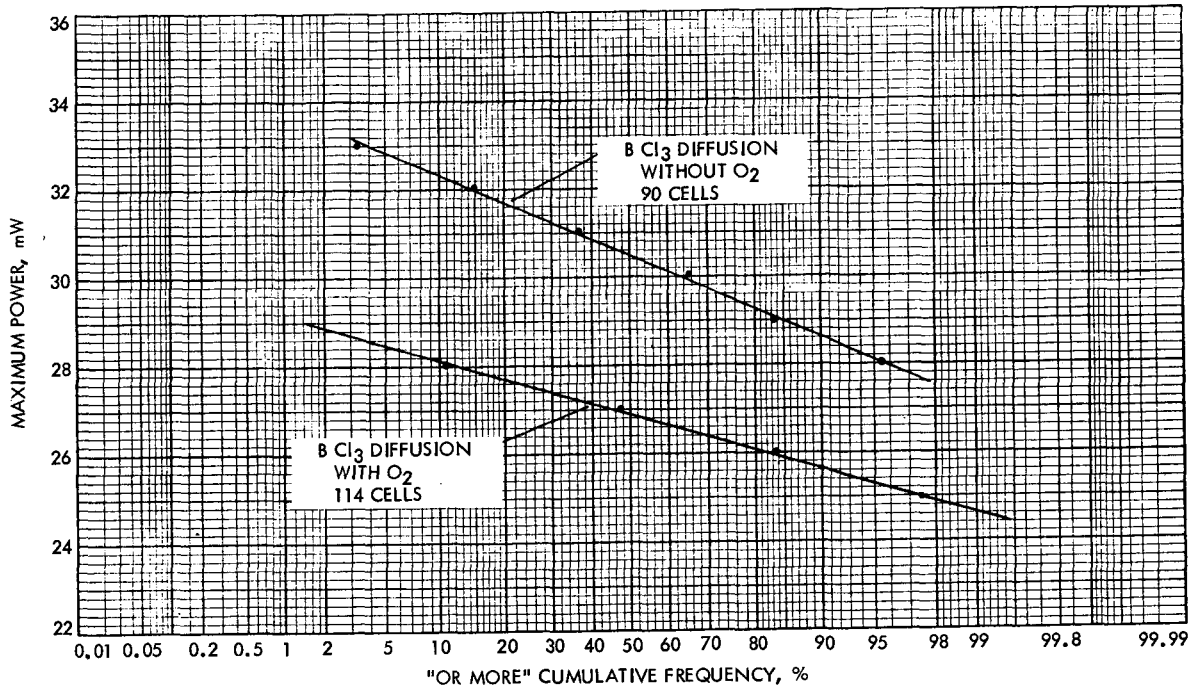

Fig. 1. Maximum power distributions for 1 Ω-cm P/N cells diffused with two different boron diffusion techniques (measured at 25°C in solar simulator at 140 mW/cm^2 intensity)

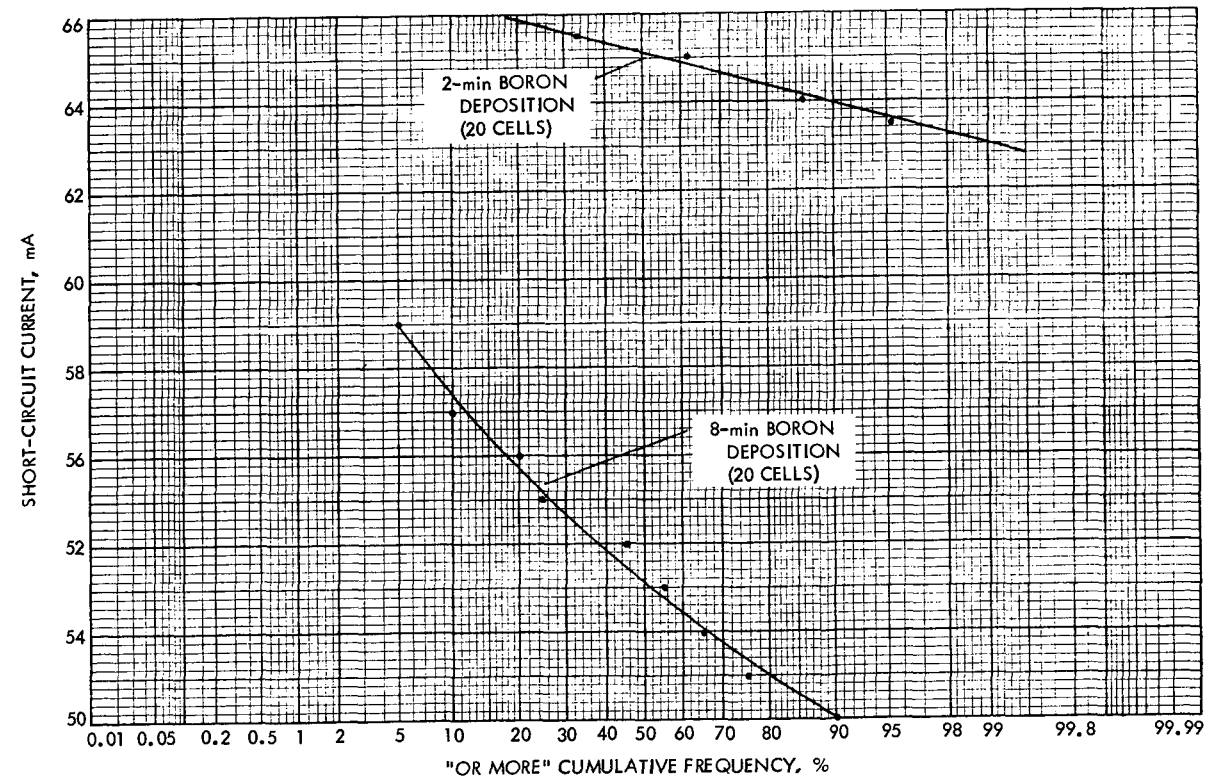

Fig. 2. Comparison of short-circuit current of lithium cells as a function of boron deposition time (measured at 25°C in a tungsten light source at 100 mW/cm^2 intensity)

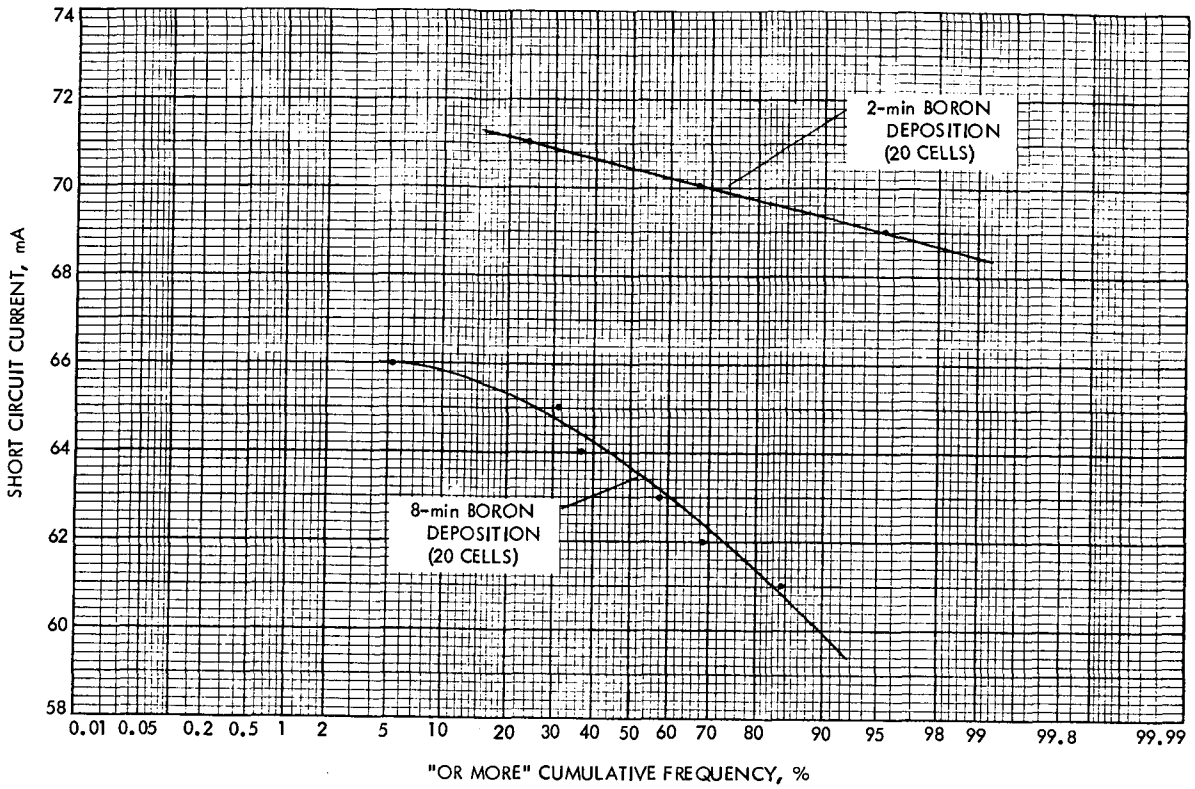

Fig. 3. Comparison of short-circuit current of lithium cells as a function of boron deposition time (measured at 25°C in solar simulator at 140 mW/cm^2 intensity)

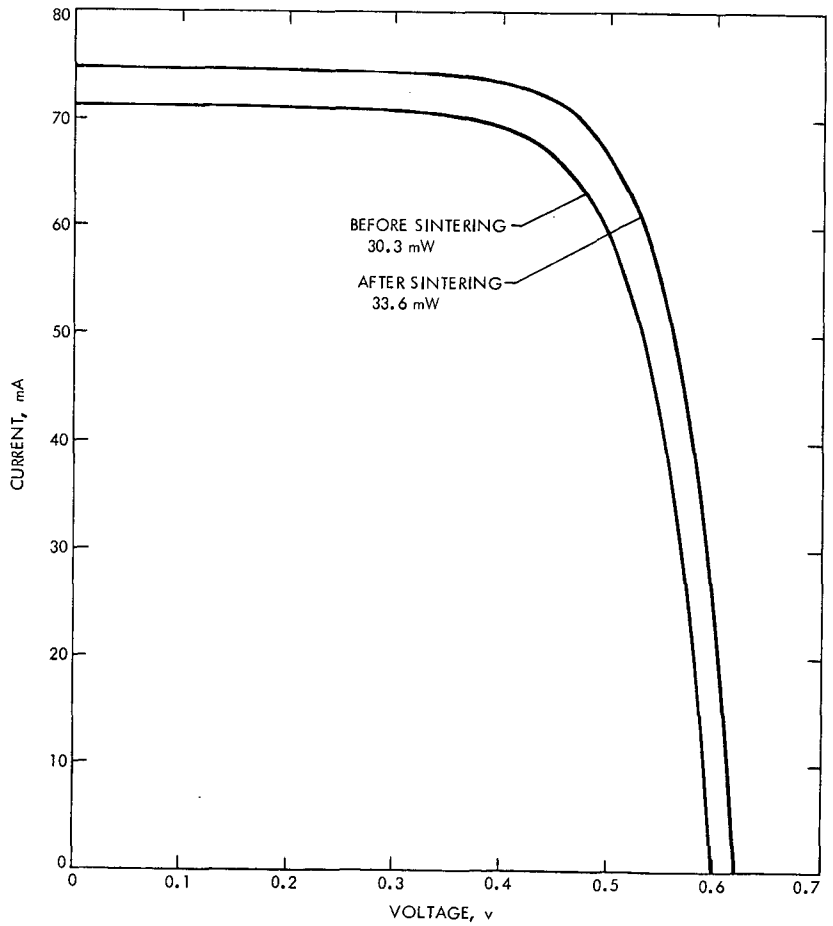

Fig. 4. I-V characteristics curves of a typical lithium cell before and after sintering (measured at 25°C in solar simulator at 140 mW/cm^2 intensity)

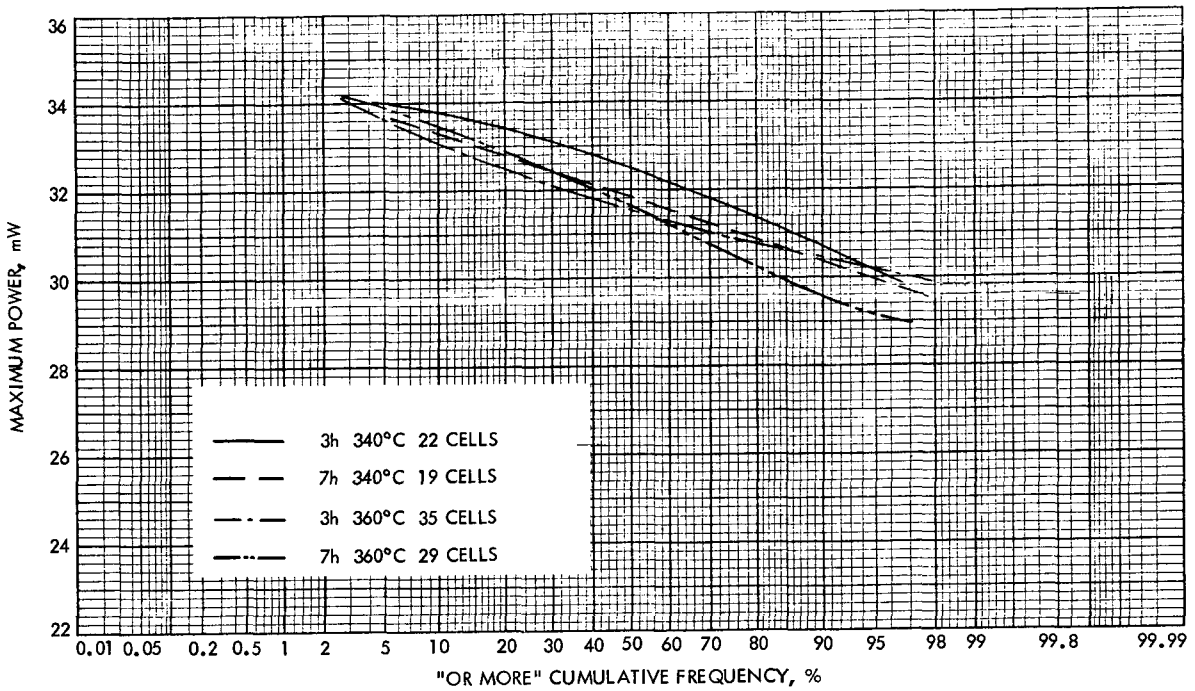

Fig. 5. Maximum power distributions of Lopex lithium fabricated for Lot 11 (measured at 25°C in solar simulator at 140 mW/cm^2 intensity)

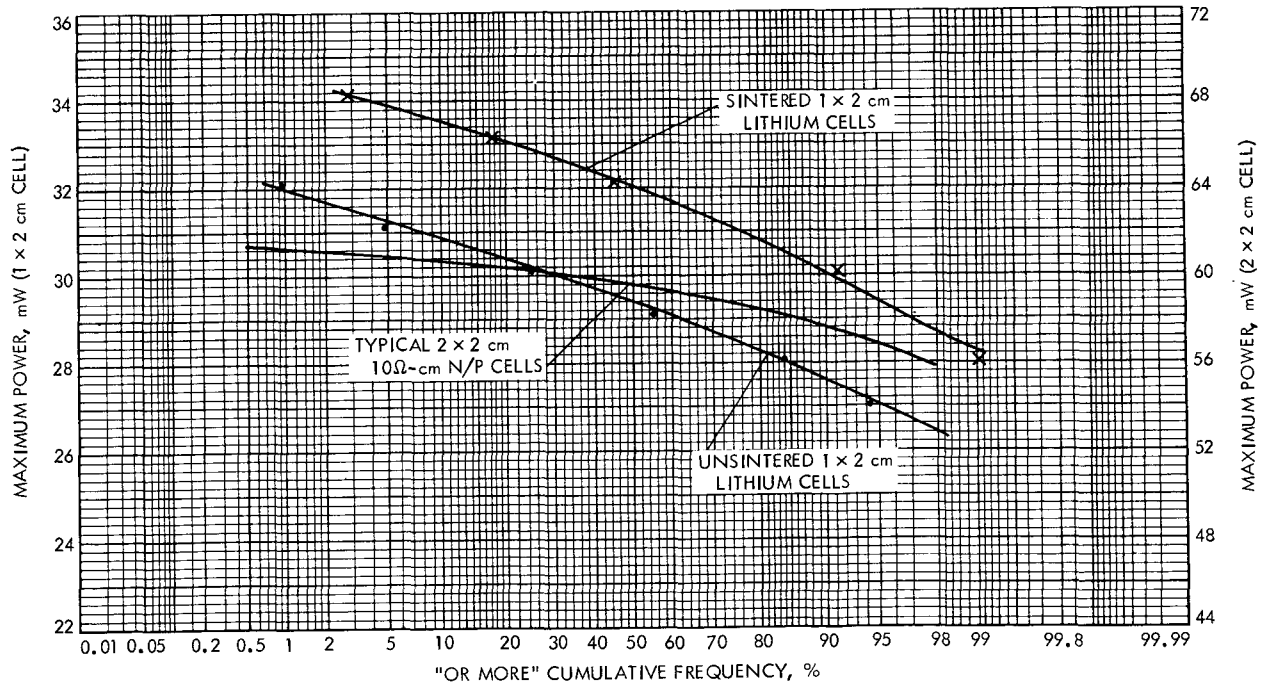

Fig. 6. Comparison of sintered and unsintered Lopex lithium cell output distributions to a typical 10 Ω-cm N/P cell output distribution (measured at 25°C in solar simulator at 140 mW/cm^2 intensity)

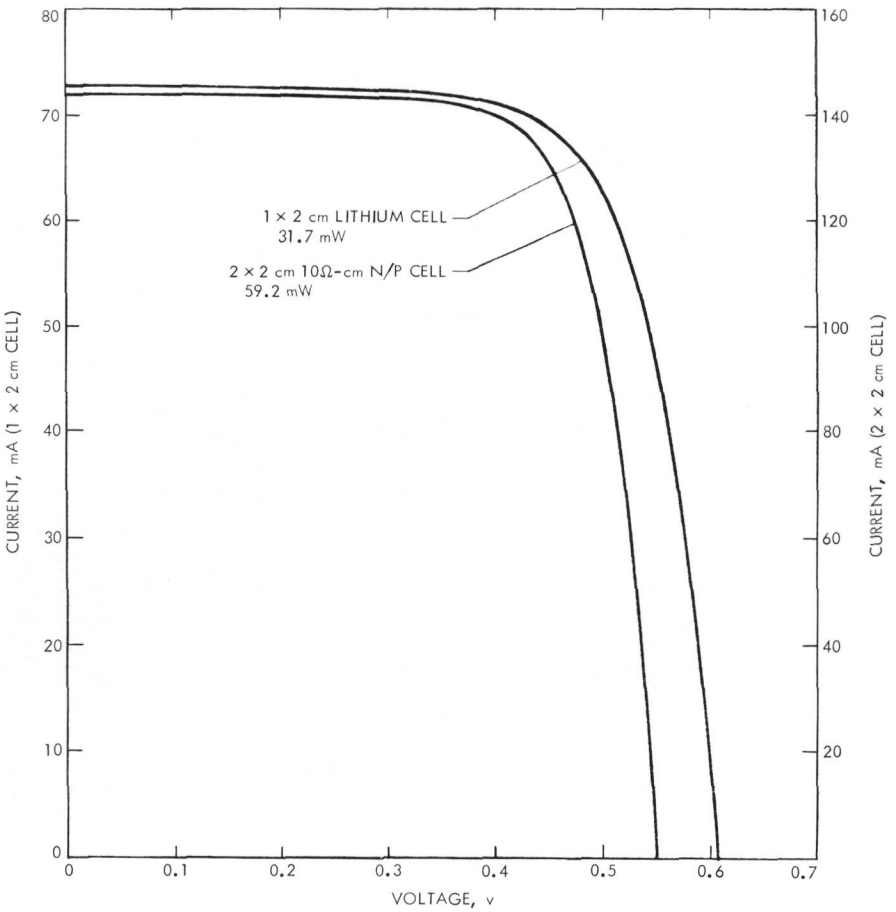

Fig. 7. Typical 10 Ω-cm N/P cell versus typical Lopex lithium cell (measured at 25°C in solar simulator at 140 mW/cm^2 intensity)

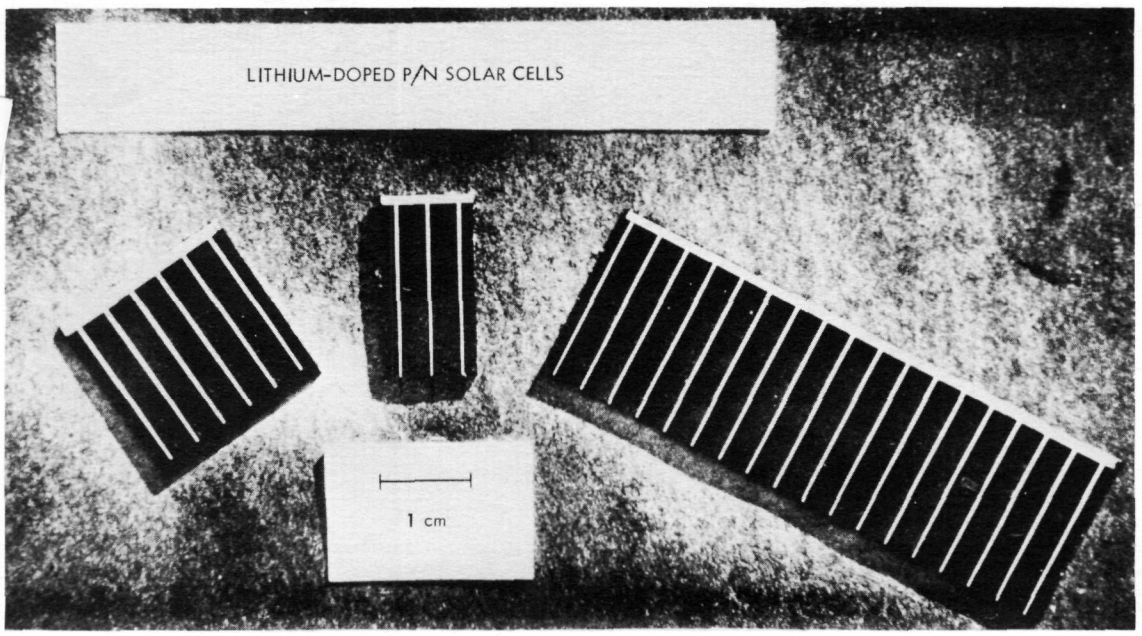

Fig. 8. Various size lithium cells fabricated by Heliotek