

HIGH TEMPERATURE STORAGE CHARACTERISTICS OF LITHIUM SULFUR DIOXIDE CELLS

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My presentation today concerns the high-temperature storage characteristics of lithium sulfur dioxide batteries. This subject was of particular interest at last year's battery workshop, since it was reported at that time that some limitations in shelf-life capability was experienced during prolonged high temperature storage.

Let me start my discussion by introducing basic problems and their historical background.

The lithium sulfur dioxide battery system has attracted considerable interest in recent years due to its wide operational temperature capability, its high energy density characteristics, and its inherent stability and capacity retention during prolonged storage at elevated temperatures.

However, as the applications for lithium SO₂ batteries expand, the performance expectations and shelf-life requirements are often extended by the potential users.

Of particular interest are recent studies directed toward quantitatively determining shelf-life limitations and the associated failure mechanisms. In the course of these studies, it was observed that corrosion of the insulated glass seal within hermetically sealed cells resulted in premature cell failure during prolonged high-temperature storage. A procedure has now been developed which eliminates or significantly retards this corrosive process.

The lithium SO₂ electrochemical system was originally packaged within a nonhermetic enclosure using an elastomeric gasket which was mechanically crimped to form a compressive seal between the cell cover and its casing.

(Figure 2-104)

However, as shown in the first figure this design allowed the gradual diffusion of sulfur dioxide over prolonged storage periods, the rate of which was dependent on cell diameter and storage temperature. For example, the SO₂ diffusion rate of a D cell was observed to be 1.3 milligrams per day at 70°F as compared to 9.6 milligrams per day at 160°F.

The effect of this SO₂ diffusion on cell performance was later verified on nonhermetic D cells stored at 70°F for a period of 6 years as shown in the next figure.

(Figure 2-105)

These results demonstrated a capacity retention of 85.8 percent, which is equivalent to a decay of approximately 2.4 percent per year; a reduction which correlates primarily to the loss of sulfur dioxide.

(Figure 2-106)

The hermetically sealed lithium SO₂ cell as shown in the figure was subsequently developed to eliminate the SO₂ diffusion and to improve overall capacity retention to all temperatures. This design incorporates as a positive terminal, an insulative hermetic glass seal located within the top structure of the cell. The glass seal consists of a central terminal and a steel body which are fused to a glass preform to effect an hermetic compressive seal, the leak rate of which has been measured to less than 2×10^{-8} cc's per second of helium.

Cells of this construction were subsequently stored at 160°F for 1 year, and capacity measured at periodic intervals.

(Figure 2-107)

The results indicated in the figure show an initial capacity loss of approximately 15 percent during the first 2 months, followed by a period of relative stability through the ninth month. However, at the twelve-month interval, the remaining cells were not able to support a resistive load, in this case, 1.9 ohms, and subsequent analysis showed the cells to be in a state of complete discharge.

Upon examination of these discharged cells, it was observed that the glass seals were severely corroded across its insulated surface. Subsequent analysis of this corrosive material showed evidence of lithium deposited within the glass structure, presumably by a replacement mechanism with metallic fillers present within the glass structure. Such corrosion apparently resulted in the formation of a conductive path across the insulative glass causing parasitic self-discharge of the cell.

An extensive program was subsequently conducted to characterize this specific failure mechanism and to institute appropriate corrective action. Alternative glass formulations and selected glass barrier coating materials were evaluated within cells stored for prolonged durations at 185°F, an increased temperature level that was selected to accelerate the corrosive reaction.

Candidate materials were analyzed alongside control samples for comparative study. Acceptance criteria for an effective barrier material included the following:

First of all, stability within the electrolyte; second, surface adhesion over a broad temperature range; third, a suitable viscosity for application of the coating; and finally, satisfactory dielectric properties.

While some glass formulations appear to perform better than others, all eventually showed evidence of corrosive degradation after 12 weeks storage at 185°F.

Successful results, however, were achieved using a two-part barrier coating material, which was applied to the internal surface of the glass seal and was cured under a predetermined thermal profile. The results obtained on cells utilizing coated seals versus uncoated control samples are illustrated in the next group of figures.

(Figure 2-108)

Before I comment on these photographs, let me just make a few general observations. First of all, the corrosion process on uncoated samples appears to be electrochemical in that it propagates radially from the seal body toward the central positive terminal as a function of storage time.

The coated seals, however, remained intact throughout the test period and exhibited no evidence of embrittlement or degradation. Subsequent removal of the barrier coating showed the glass surface completely intact and free of corrosion.

Now, this figure shows two groups of cells: one with an uncoated glass-to-metal seal that is shown on the left side, and those cells with a coated seal as shown on the right. As you can see, at week number 4 at 185°F, the corrosive reaction is well underway. And as you can see in the left photograph, it is emanating from the body of the glass-to-metal seal toward the central terminal.

As you can see in the right-hand photograph, the coated seal is free of any embrittlement or cracking. The adhesive bond is in excellent condition. When the coating is physically removed, the glass appears to be in its original state.

(Figure 2-109)

Here we are at week number 8. As you can see, the corrosive material has almost completely covered the insulated glass surface on the two left photographs. But, as you can see on the right, the coated seal remains intact, and physical removal of the coating shows the glass to be again in its original condition.

(Figure 2-110)

This is week number 10. At this time, the uncoated seals are completely covered with the corrosive material, and a conductive path has now formed from the body of the eyelet to the central terminal. This is the point of time in which I describe the resulting parasitic self-discharge phenomenon. Within a fairly short period of time, the cell has completely discharged once the seal is in this corrosive state.

Again, on the right-hand view, we see that the coated seal again appears to be completely intact and free of any corrosive material. Upon removal of this coating, the glass seal is again free of any evidence of corrosion.

(Figure 2-111)

This was the final week of the study. This was 12 weeks at 185°F. By this time, the corrosion has not only covered the insulative surface, but has even started to migrate up the central terminal of the glass-to-metal seal. This sometimes results in open circuit of the cell if the discharge has not been completed by this point in time.

The coated samples again showed no evidence of corrosive attack, even after 12 weeks at 185°F. Again, removal of the coating at this point in time shows the seal to be in its original condition without any evidence of cracking or deterioration.

Capacity retention data for these test cells are shown in the next figure.

(Figure 2-112)

Control samples with uncoated seals showed a slight loss in cell capacity after 2 weeks storage at 185°F, followed by a pronounced loss after 4 and 6 weeks, and were unable to support a resistive load after eight weeks.

Examination of these cells indicated that self-discharge of the cell had occurred. Cells containing coating seals, however, were extremely stable by comparison and delivered approximately 85 percent of initial capacity after 12 weeks' storage at 185°F.

This data clearly demonstrates the effectiveness of the barrier coating in preventing glass-seal corrosion with the resulting improvement of shelf-life characteristics and overall capacity retention at elevated temperatures.

In conclusion, it can be seen that the development of hermetically sealed lithium SO₂ cell eliminated the problem of SO₂ diffusion and its adverse effects on shelf life. However, successful use of this hermetic design requires that the problem of glass-seal corrosion be addressed, specifically the resulting parasitic cell self-discharge phenomenon.

An effective solution to this problem has been developed, which will significantly enhance the overall reliability, shelf life and capacity retention characteristics over a wide temperature spectrum. This new development will now permit successful implementation of the lithium SO₂ system in many new and more demanding applications and environments.

DISCUSSION

BENNETT: I want to thank you for doing this study as a result of some of the questions I raised last year. But, were these done in the invert, or were these upright?

WATSON: We conducted some tests in various orientations, both with the central terminal up-down, as well as horizontal. We found that the worst-case condition occurred with the terminal in the down position, although in all cases the corrosive reaction occurred. In some cases it would take 8 weeks; in some cases 10 weeks. But it was just a matter of time before the corrosion resulted, regardless of the orientation of the cell.

BENNETT: I was rather curious about the fact that you said in every case the corrosive product was conductive. As I mentioned last year, I had some cells that were on at 140°F for 3 1/2 years. In no cases was the corrosive product conductive, even though 60 percent of the glass seal was gone after that period of time.

Do you have any comments on that?

WATSON: The results of the testing that we have conducted showed, in all cases in the cells that we tested, partial discharge of the cell had occurred. In some cases it was not complete discharge. The resistive path in some cases is quite high, and the length of time for the cell to be completely discharged, especially a large-size cell with a lot of capacity, might take longer than the test period which you ran.

Most of the cells we ran our tests on were primarily 1-ampere per hour and 8-ampere per hour cells. And the phenomenon seemed to show itself up fairly quickly.

VASANTH: My first question is, which method was used in order to detect the corrosion; chemical, visual, or microscope?

WATSON: We initially used a visual examination to determine that it was electrochemical. I don't know how all the photographs appeared from where you sat. But it does clearly show, if you look at them closely, that the corrosive material does migrate radially from the sealed body towards the central terminal.

Now, if this were a chemical versus electrochemical type of phenomenon, I would expect to see the corrosive material occur in random positions along the glass surface. But in all cases it became radial from the outside in.

VASANTH: Did you also measure the rate of corrosion by weight loss method?

WATSON: No. The rate of corrosion was done by a visual observation: by disassembling and examining the cells and observing and photographing the condition of the glass-to-metal seal at various intervals throughout the test.

VASANTH: In other words, it was only qualitative?

WATSON: Qualitative. But we also ran capacity tests, as I showed in the previous figure which showed that the capacity retention was significantly affected as the storage life progressed.

VASANTH: My last question is, have you tried some methods that would suppress the corrosive reaction?

WATSON: I am sorry, would you repeat that?

VASANTH: Corrosive reactions can be suppressed by adding some compounds that would inhibit the reaction. Have you tried some of those?

WATSON: No, we haven't tried any inhibiting materials to add to the electrolyte because we are not quite sure what the mechanism is that is causing this to occur.

We have experimented, and some of the manufacturers of the glass-to-metal seal have experimented with various glass formations. But, to date, they have not been too successful. As I mentioned, some are somewhat better than others, but in all cases, after 12 weeks the corrosion had occurred.

HESS: Can you comment on the recent lithium battery failure that occurred in Bermuda?

WATSON: Yes. I can give you some information on that. As you are probably aware, a complete investigation of that incident is presently being conducted, and I wouldn't want to speculate on the specific causes nor the corrective action that might result from that investigation. But I can give you some limited information based on a preliminary study which I believe has just recently been completed.

That particular incident you referred to was an explosion which occurred or violent event which occurred on a lithium battery incorporating seventy-two 30-ampere hour cells. These were packaged in a series parallel relation with protective fuses and diodes. These cells were hermetically sealed both with a venting mechanism. In fact, in this particular case it was a dual vent to provide a backup safety vent mechanism.

Some of the findings that were determined, at least to date, showed the following:

First of all, the packaging of the battery was done by the user. The user did not follow the specific instructions as recommended by the manufacturer.

There were no provisions for venting any overpressurized electrolyte or gases that might result due to a cell or group of cells venting.

Second of all, the construction of the battery pack itself was a very strong reinforced cylindrical type of container which was not designed to withstand some of the shock and vibration that this battery was subjected to during its use in storage.

Thirdly, and I think most important, is that the user did not follow the recommended guidelines for discharge of the battery. Specifically, the battery was discharged well below the recommended capacity and voltage limitations that were set up by the manufacturer.

JOHNSON: You said that most of your tests were conducted at elevated temperatures. Did you also run control specimens at a low temperature, at room temperature? And if so, could you make a comment as to the rate of corrosion at the higher temperature versus the room temperature?

WATSON: That's a good question. We have done tests both at room temperature and elevated temperatures. Obviously, we have done the elevated temperatures or have concentrated on these primarily because of the time function.

We do have some correlation between 185°F storage versus 160°F storage, again based on visual observations of the glass seal. As you saw from some of my data, 8 weeks or 10 weeks at

185°F is roughly equivalent to approximately 9 months at 160°F. Again this is based on what we observed.

We have not had this glass seal coating for that long a period of time that we could really determine whether it is benefiting us at room temperature. To date, the longest hermetically sealed cells that have been stored are roughly on the order of 3 to 4 years. And in no cases have I observed any significant evidence of corrosion.

So right now I don't have a correlation between what happens at room temperature versus what happens at elevated temperature. But it may be that further studies along about 7 years at room temperature may show up this relationship.

BENNETT: I would like to answer that question somewhat, if I may. Last year we tore apart hermetically sealed lithium sulfur dioxide cells that had been on storage for 3 1/2 years at 140°F, 70°F, and 0°F. We evaluated the quality of the glass seal and the amount of the corrosion product by immersing it in water and collecting the amount of hydrogen gas that was involved. So we had a fairly accurate comparison between them.

The ones that were at 140°F for 3 1/2 years had about 60 percent of the glass, shall we say, dissolve. The ones at 70°F had less than 1 percent. And the ones that were at 0°F were in new condition. That might give you some idea as to what the comparison is between temperatures.

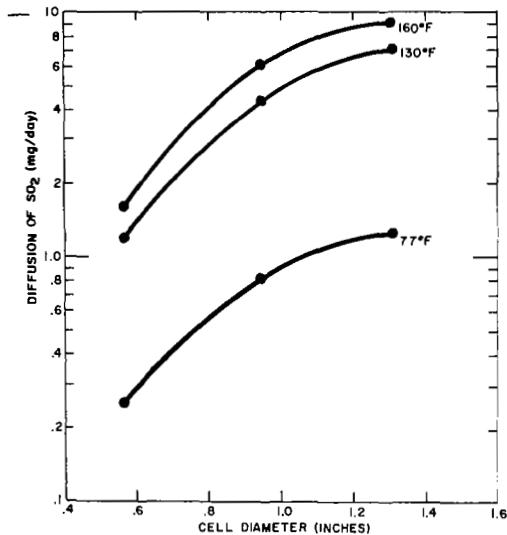


Fig. 1 Diffusion rate through elastomeric seal

Figure 2-104

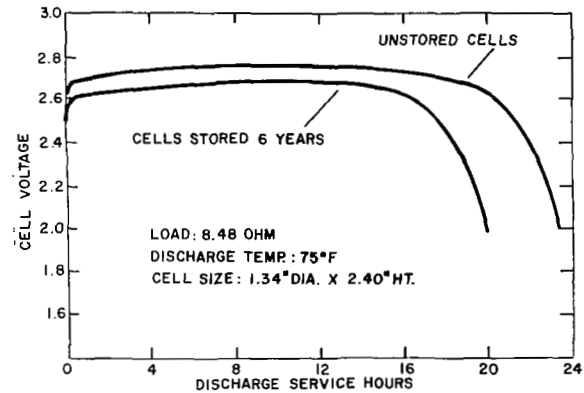


Fig. 2 Shelf life of non-hermetic cells (elastomeric crimp seal)

Figure 2-105

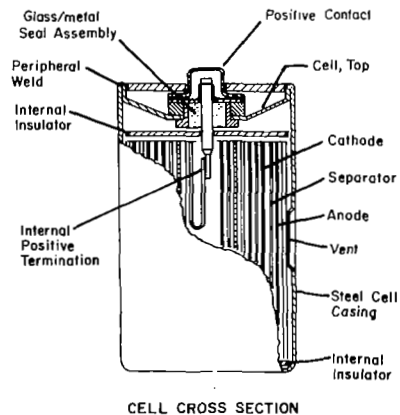


Fig. 3 Hermetically sealed Li/SO₂ cell

Figure 2-106

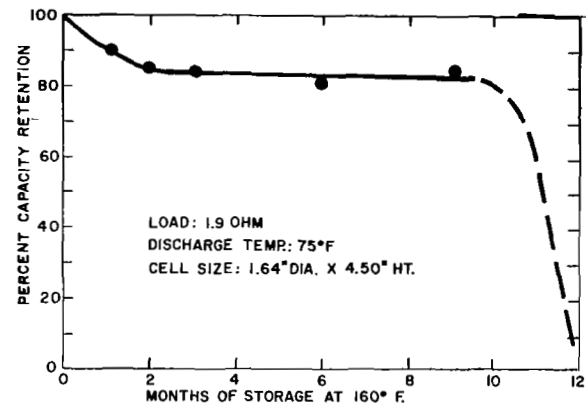


Fig. 4 Shelf life of hermetic cells (without high temperature seal)

Figure 2-107

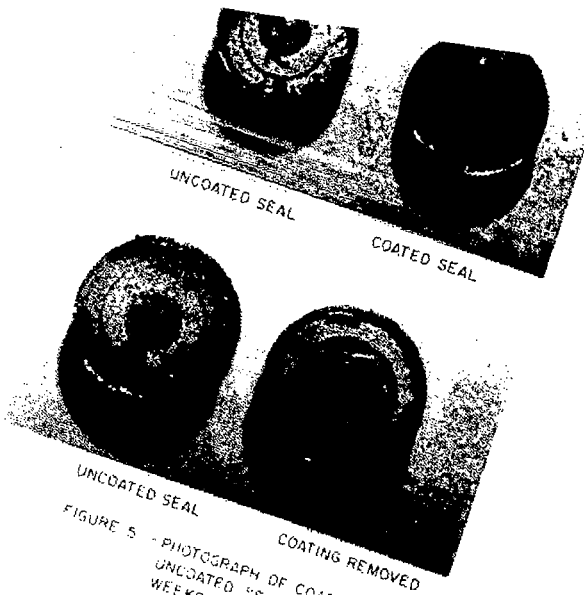


FIGURE 5 - PHOTOGRAPH OF COATED AND UNCOATED SEALS AFTER 4 WEEKS AT 185°F

Figure 2-108

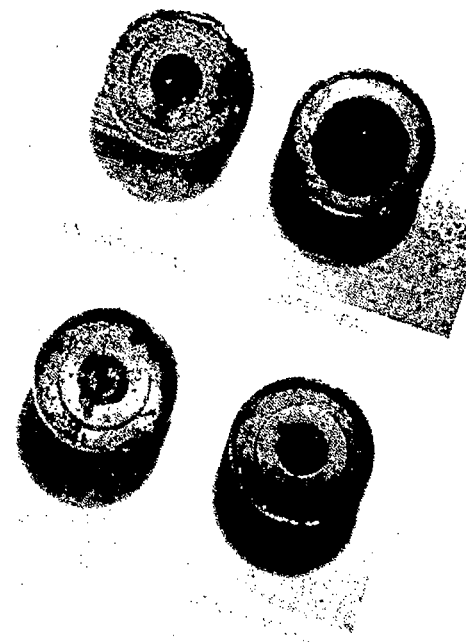


Figure 2-109

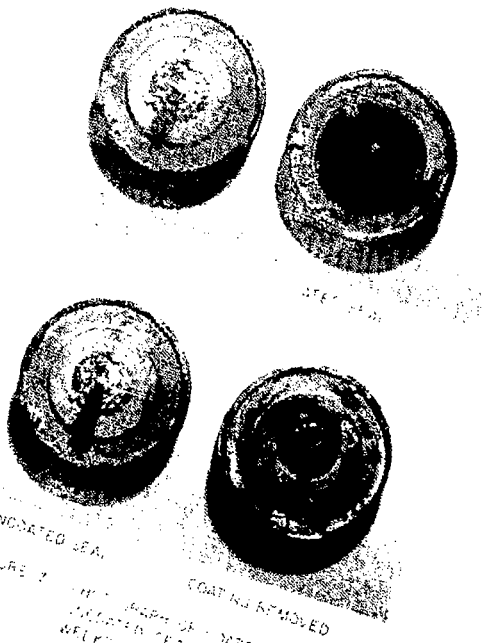


FIGURE 7 - PHOTOGRAPH OF COATED AND UNCOATED SEALS AFTER 12 WEEKS AT 185°F

Figure 2-110

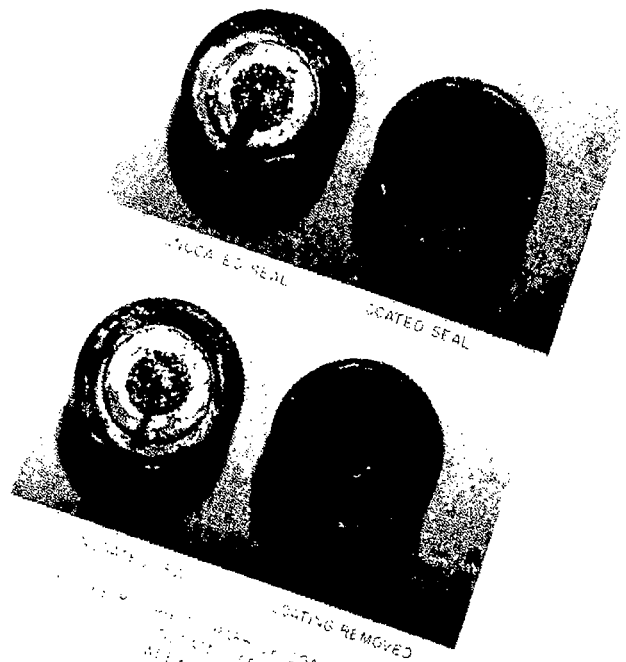


FIGURE 8 - PHOTOGRAPH OF COATED AND UNCOATED SEALS AFTER 12 WEEKS AT 185°F

Figure 2-111

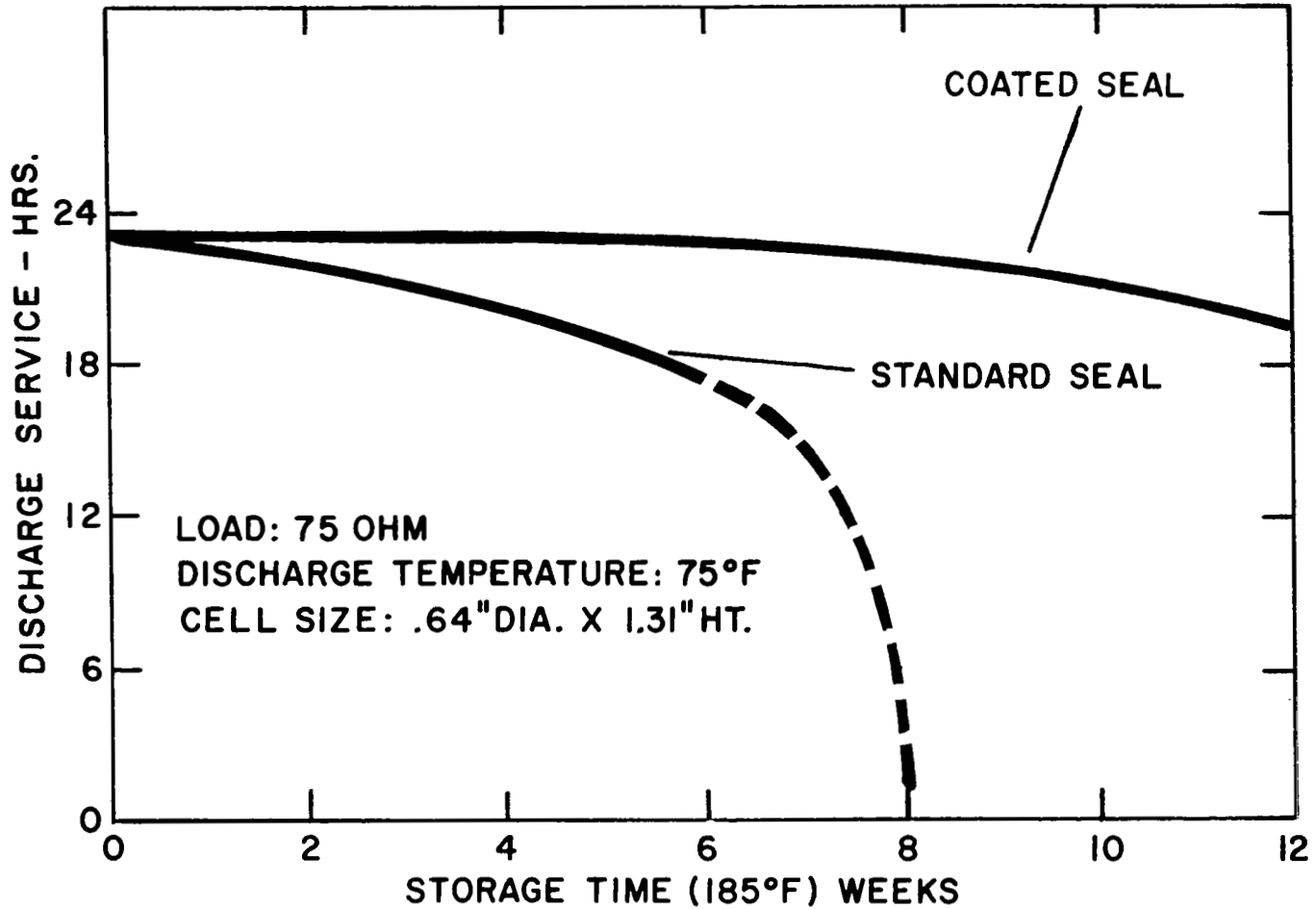


Fig. 9 Comparison of storage (with & without coating)