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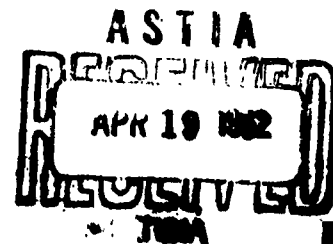
FIFTEENTH QUARTERLY TECHNICAL PROGRESS REPORT

Feasibility Study on High Performance,  
Short Duration Power Batteries

Contract NOrd-18240

December 15, 1961 to March 15, 1962

Research Laboratory of  
Union Carbide Consumer Products Company  
Division of Union Carbide Corporation  
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Purpose

Determination of the feasibility of producing batteries far exceeding present performance as typified by the following examples:

1. 100 KW for 15 minutes, as in torpedo propulsion applications, with an energy density of 250 WH/lb, or 19 WH/in.<sup>3</sup>
2. 10 KW for 5 minutes with an energy density of 100 WH/lb or 7.5 WH/in.<sup>3</sup> as in guided missile auxiliary power applications.

Summary

In July 1958, a research program designed to determine the feasibility of producing a very high power density battery system was initiated. An initial survey of various types of battery systems had indicated that if one made reasonable assumptions regarding the operating efficiency and size of the system, its operating temperature would be in the range of thermal batteries employing fused salt systems as the electrolyte. While such thermal battery systems are known, they operate at very low efficiencies. The first step in this investigation, therefore, was the calculation of the theoretical output of a large number of thermodynamically feasible systems. The systems which were shown by these calculations to be theoretically capable of producing the required power density were investigated further.

Since the cathodic portion of any thermal battery is generally agreed to be the limiting element, and since anodic reactions are better understood than cathodic reactions, the investigation was confined to the examination of potential cathodic materials. The power density specifications as set forth above were used to determine the volume of the battery, and from this, assuming an overall efficiency of 50 per cent, a simple cubic shape and black body radiation, the battery operating temperature was calculated as being approximately 1100°C. Since such a temperature would lead to a host of prob-

lems, not only with the battery components themselves, but also with the materials of construction, a lower operating temperature is necessary. This can be achieved by adding radiation fins to the battery case and in other ways increasing the surface to volume ratio. When these conditions are attained, it will be feasible to operate in the 600-900°C range.

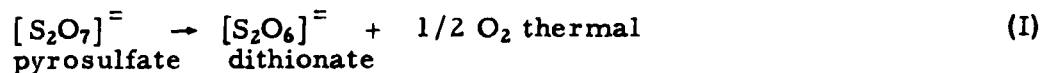
In the investigation of potential cathodic materials, the first determination was that of the solubility, in the battery electrolyte, of those compounds which were thermally stable in the temperature range from 600 to 900°C. The materials which showed appreciable solubility were eliminated, since they would tend to give poor service due to direct chemical reaction with the anode. Two electrolyte systems, KCl-LiCl eutectic and  $K_2SO_4$ - $Li_2SO_4$  eutectic were used in these tests.

After the solubility determinations had been made, those materials with only limited solubilities were examined for their potential vs. current relationships. These tests were made to determine the electrode potential at which reduction occurs. Electrolysis of the materials was then carried out at that electrode potential in order to obtain sufficient quantities of the reduction product for identification. When these tests were carried out with the halide eutectic, the reductions occurred at different potentials, as was expected. In the sulfate melt, however, it was observed that the plateaus in the curve occurred at the same potentials, regardless of the cathode material present, or even in the absence of any such material. At the same time, it was noted that at the conclusion of each such run, the cold melt had an odor of sulfide. The indications, therefore, were that the sulfate ion was being reduced to the sulfide ion. Since a reduction of sulfate to sulfide would give far more power per pound than any of the other materials previously considered as depolarizers, it seemed appropriate to attempt to determine the mechanism for the reaction, considering the sulfate as a depolarizer rather than as an electrolyte.

Chronopotentiometry, the study of the change of potential of a system with time, at a fixed current, was chosen as the method to be used for the investigation of the sulfate reduction mechanism. The total time of the current

pulse for each chronopotentiogram is of the order of 10 to  $10^3$  milliseconds. From the battery standpoint, such an investigation may be viewed as the effect, on the cathode, of a constant current discharge, with the total time in a range such that the process is subject to rigorous mathematical analysis. Most previous chronopotentiometric investigations in molten salts have been confined to temperatures of  $450^\circ\text{C}$  and below. In this case, however, since the battery operating temperature will be  $600\text{-}800^\circ\text{C}$ , these tests were all made on the  $500\text{-}900^\circ\text{C}$  range. Because the concentration of the material being investigated is kept very low, the presence of impurities in the melt can lead to confusing results, unless the effect of such impurities can be ascertained beforehand. Therefore, the first materials which were investigated were potential impurities, such as oxides, hydroxides, silicates, aluminates, etc.

Of the potential cathodic materials, the sulfate ion has been investigated most extensively to date. Since the ultimate reduction product is sulfur or a sulfide, oxide ion is also a product of the cathode reaction. The mechanism by which these products are obtained is not a simple one, however. Chronopotentiometric analysis of sulfate dissolved in KCl-LiCl indicated that the quantity of material available for reduction at the cathode increased with increasing current density. This would be true if there were two types of reactions proceeding concurrently, one a thermal degradation, the other the electrochemical reduction. For example,



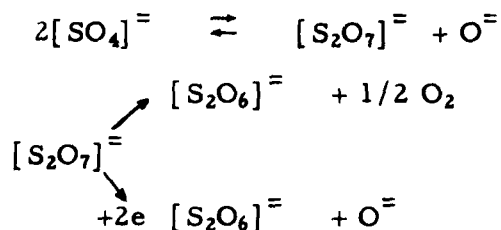
Since, at any temperature, the rate of depletion of the reducible substance by the thermal reaction is constant, it follows that the amount available for the production of power by the electrochemical reaction increases with increasing rate of reaction (II), (i. e., increasing current density).

The chronopotentiometric measurements also showed that oxide ion decreased the concentration of the reducible substance. This suggests that

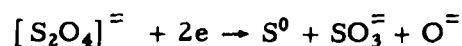
the reducible substance and oxide are both reaction products in some equilibrium system. For example,



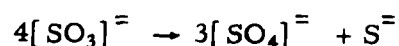
Finally, the magnitude of the values of  $\frac{i\tau^{1/2}}{C}$  in the chronopotentiometric measurements indicated a two-electron reaction if the diffusion coefficient of the reducible species is assumed to be equal to that of other divalent ions (i. e.,  $\text{Cd}^{2+}$ ) previously measured in this system. The following then is the proposed mechanism based on the information obtained to date:



The dithionate ion  $[\text{S}_2\text{O}_6]^-$  is written here only as an example of the many compounds of sulfur of valence less than 6 which may be formed. All, however, are less stable thermally than sulfate (or pyrosulfate) and would disproportionate to produce more hexavalent sulfur ions and ions of still lower valences. This process may continue until hydrosulfite ( $\text{S}_2\text{O}_4$ )<sup>-</sup> is reached. This ion has considerable thermal stability at these temperatures and is reduced at a potential close to that of sulfate (or pyrosulfate). It is believed then that another two-electron electrochemical reduction occurs, viz:



with the sulfite ion going through a disproportionation process to produce sulfate ion, which will again go through the above reactions, and sulfide ion,



While much of this remains to be proved, it is consistent with the data available.

Other common oxygenated anions, stable at ordinary temperatures, such as phosphates, silicates, borates, and carbonates, have also been investigated. The carbonate ion behaved peculiarly in that it was quickly lost from the melt. This would seem to indicate a thermal instability, but analysis of

the effluent gas for  $\text{CO}_2$  and other carbon-containing gases showed that only 10 - 12 per cent of the carbonate was lost by decomposition. It is possible that a stable chlorocarbonate anion which is difficult to reduce may be formed in this system. No mechanism has been worked out for the phosphates, silicates or borates, although phosphorus is known to be the end product of the phosphate reduction.

These anions appear to be characteristic of a new class of potential cathode materials. Consequently, the theoretical outputs of a number of cells involving various types of such oxygenated anions have been calculated, and it has been found that high coulombic capacities and power densities characterize the entire group.

A group of test cells involving  $\text{Sb}_2\text{O}_3$ ,  $\text{CuO}$ , borates, silicates, sulfates and phosphates were made up for screening purposes and evaluated. Initially, Kaolin clay, which has been used as a separator in thermal cells by others, was used in making these cells. However, Kaolin is an aluminosilicate and thus an oxygenated anion stable at ordinary temperatures. It is, therefore, capable of itself acting as a depolarizer. However, it was found that the insoluble residue which remains after the Kaolin in the separator is reduced interferes with the reduction of  $\text{Sb}_2\text{O}_3$ , or  $\text{CuO}$  when they are used as depolarizers. When fused  $\text{MgO}$  was used as a separator, the cell output was increased more than threefold in some instances. Cell output, based on the anode (generally calcium) weight, plus the calculated amount of cathode material for complete reaction, ranged up to 232 WH/lb with  $\text{CuO}$  as the depolarizer and to 132 WH/lb with  $\text{Sb}_2\text{O}_3$  as the depolarizer. In the case of the oxygenated anion depolarized cell, the combination of a calcium anode with a  $\text{CuSO}_4$  depolarizer consistently gives a power output of 300 WH/lb based on active material. Similar cells using  $\text{Fe}_2(\text{SO}_4)_3$  as the depolarizer attained 415 WH/lb. With  $\text{KPO}_3$ - $\text{LiPO}_3$  eutectic as the depolarizer, 320 WH/lb has been attained.

The above figures are based only on active material weight (anode plus cathode); when the figures for a total balanced cell are compared, the Ca- $\text{CuO}$  combination gave 182 WH/lb; Ca- $\text{CuSO}_4$  gave 140 WH/lb; Ca- $\text{Fe}_2(\text{SO}_4)_3$  gave 210 WH/lb and the Ca- $\text{KPO}_3$ - $\text{LiPO}_3$  combination gave 220 WH/lb.

In the chronopotentiometric work on the mechanism of the reduction of sulfates, it was necessary to assume a value for the diffusion coefficient of the sulfate ion. Since the conclusions regarding the mechanism depend to some extent on the accuracy of this assumption, it was deemed advisable to measure the diffusion coefficient of the sulfate and phosphate ions in the alkali-halide eutectic. Also, since it is likely that material transport will be the ultimate limit on the rate of the electrode reactions, knowledge of the diffusion coefficient of the reactants would be of considerable importance in optimization of the cell.

A preliminary measurement of the diffusion coefficient of Ag ion was made to check the apparatus and method, and agreement within 10 per cent was found with a value determined chronopotentiometrically at Argonne National Laboratory. However, chemical analysis used in this work was too insensitive and radiochemical methods were found to be necessary.

Attempts to measure concentration gradients in a capillary after diffusion, using radioactive tracer techniques, failed since the gradient was upset during the cooling process. Consequently, the total silver content of the diffused samples was measured using a pulse height analyzer and scintillation detector. These data were then used to calculate the diffusion coefficient for silver at temperatures ranging from 450 to 825°C.

#### Abstract

Some 72-hour diffusion runs involving silver were made to finish this work. The data were used to calculate  $D$  and  $\Delta H$  for the diffusion process.

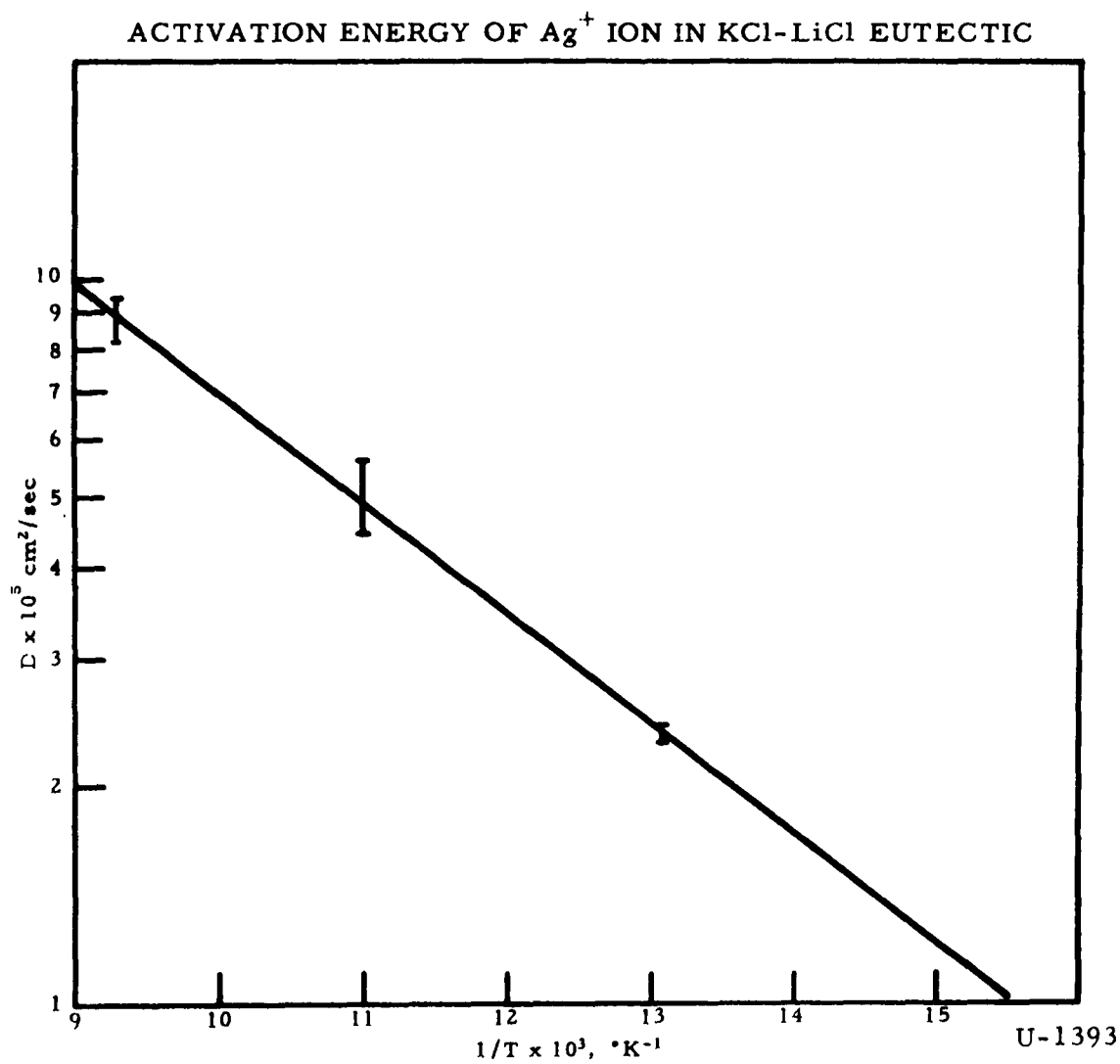
The work on measuring the diffusion coefficient of phosphate ion was started but it was found that the data obtained were very erratic due to the low solubility of the ion. While this problem is being overcome, the diffusion coefficient of the sulfate ion will be measured.

A number of cells involving sulfates or phosphates as both depolarizer and electrolyte were made and tested. The best of the phosphate cells involved  $\text{LiPO}_3\text{-Cu(PO}_3)_2$  as the depolarizer and gave 265 WH/lb of active materials. Cells involving  $\text{K}_2\text{SO}_4\text{-Li}_2\text{SO}_4$  gave 110 WH/lb of active materials.

Discussion

The work on the measurement of the diffusion coefficient,  $D$ , of silver in a KCl-LiCl melt was completed with a number of 72-hour runs at various temperatures. From these data and those obtained from the previous runs, the values for  $D$  were calculated. The activation energy for diffusion was obtained from a plot of  $\log D$  vs.  $\frac{1}{T}$  shown in Figure 1.

FIGURE 1



The value of the activation energy thus determined, 3.95 Kcals, differs from that of Gruen (private communication) by less than 2.5 per cent and the values of the diffusion coefficient fall between those of Gruen (private communication) and those of Laitinen.\* It was thus established that: (1) there is no observable difference between the "polarographic" (or electrochemical) diffusion coefficient and the field-free diffusion coefficient and (2) our method and apparatus are satisfactory for the measurement.

With the completion of the silver measurements, the work on measuring the diffusion coefficient of  $\text{PO}_3^-$  was started. Radioactive phosphorus,  $^{32}\text{P}$ , was obtained as an orthophosphoric acid solution from Oak Ridge. This, in turn, was mixed with additional  $\text{H}_3\text{PO}_4$  and partially neutralized to  $\text{KH}_2\text{PO}_4$  with potassium carbonate. The  $\text{KH}_2\text{PO}_4$  was converted to  $\text{KPO}_3$  by heating to  $260^\circ\text{C}$  and then converted to the cyclic trimer by heating at  $580^\circ\text{C}$  for 5 hours. Four concentrations of phosphate ranging from .002 to .02 gram of  $\text{PO}_3^-$ /gram of  $\text{KCl-LiCl}$  melt were prepared. These were used to fill the diffusion capillaries. Additional melts, containing half the capillary concentrations, were prepared for use as the material into which diffusion was to take place. The diffusion temperatures were 500, 600, 700 and  $800^\circ\text{C}$  and the diffusion times were in the vicinity of 72 hours.

Measurement of the radioactivity of the diffused and non-diffused capillaries was again carried out with the scintillation counter.  $^{32}\text{P}$ , however, is a  $\beta$  and not a  $\gamma$  emitter, consequently the emission being measured was the X-ray emission due to absorption of  $\beta$  rays in the sample and container.

Samples which had been allowed to diffuse at  $500^\circ\text{C}$  gave average values for  $D$  which seemed to vary roughly with the  $\text{PO}_3^-$  concentration. Above this temperature, there was no correlation between concentration and the values of  $D$  obtained. In all cases, however, triplicate runs were not reproducible in both the diffused and undiffused samples and it was thought that the potassium salt might be low in solubility. Consequently, the sodium salt  $(\text{NaPO}_3)_3$  was prepared in the same manner as the  $(\text{KPO}_3)_3$  previously described.

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(\*) Laitinen, H.A. & Ferguson, W.S., Anal. Chem. 29, 4-9 (1957).

Two diffusion runs were made using the sodium salt at a concentration of 0.008 gram  $\text{PO}_3^-$ /gram of melt. The diffusion temperatures were 640 and 765°C. Again, however, triplicate samples varied by as much as a factor of three.

During the process of filling the capillaries for diffusion, it had been noted that the melt seemed to have a tendency to form a crust. This crust formed regardless of the melt temperature, which ranged from 490 to 790°C. The melt was kept under a constant nitrogen atmosphere except when capillary tubes were being filled or removed. When a melt was kept in a nitrogen filled tube for long periods of time, the melt surface cleared up, but as soon as the container was opened for viewing, even though a stream of nitrogen still passed through the vessel, crystals could be seen growing on the melt surface. Thus, the crystal growth could have been due to disturbing a super-saturated solution. The  $\text{NaPO}_3$  containing melt was filtered at 580°C and the filtrate analyzed for phosphate. It was found that the phosphate content was 75 ppm  $\pm$  10 per cent, while the original melt had been made up to contain .016 gram  $\text{PO}_3^-$ /gram melt, or 16,000 ppm.

While this low solubility makes the measurement of the diffusion coefficient of the phosphate ion much more difficult, it is very beneficial from the battery standpoint and may help to explain why phosphate-depolarized cells have been so successful. If the cathode depolarizer is insoluble in the electrolyte contained in the separator, then it cannot pass through to react chemically with the anode. Since the oxide ion which is a product of the cathode reaction is mobile in the KCl-LiCl electrolyte, the ideal situation exists in which the cathode reactant must stay near the cathode and the cathode product can diffuse away.

The insolubility of the phosphate ion may also be a decomposition problem. When the phosphate-containing melts were being examined for crust formation, it was noted that the nitrogen stream sweeping across the melt had an acidic odor. This odor could arise by some mechanism such as



Since  $P_2O_5$  sublimes above  $250^\circ C$ , this could account for the acidic fumes. Addition of oxide to a phosphate melt should therefore decrease the loss of  $P_2O_5$  and help to maintain the metaphosphate ion concentration or, if the oxide concentration is high enough, convert the metaphosphate to the ortho compound. It was found that addition of oxide ion only served to cause more crust to form on the melt surface. In addition, an attempt to prepare an orthophosphate solution failed since a clear melt was never obtained. Additional oxide in this case only increased the amount of precipitate.

It appears that it is the orthophosphate that is the insoluble species. If this is so, some moisture contamination is required to form it. In the procedure for testing cells used thus far, moisture has not been rigidly excluded but in the diffusion studies, rigidly dry conditions were sought. It is possible, however, that it was not actually attained and additional precautions in the drying of the nitrogen atmosphere will be used in further attempts at diffusion measurements.

At present, other molten salts are being checked as solvents for the metaphosphate ion so that its diffusion coefficient can be determined. During this time, the diffusion coefficient of the sulfate ion will be determined.

A number of cells involving sulfates as both depolarizer and electrolyte were prepared. Using  $K_2SO_4$ - $Li_2SO_4$  eutectic, the best cell gave 110 WH/lb based on active material; using  $K_2SO_4$ - $CuSO_4$ , the best cell gave 161 WH/lb of active material.

Phosphates used under the same conditions gave 198.6 WH/lb when  $LiPO_3$  was used and 264.5 WH/lb of active material when a mixture of  $LiPO_3$ - $Cu(PO_3)_2$  was used.

Coulometric tests were conducted on copper sulfate depolarizers to determine whether all the energy developed could be accounted for on the basis of a two-electron change ( $Cu^{++} \rightarrow Cu^0$ ); on the basis of a six-electron change ( $S^{+6} \rightarrow S^0$ ), or on the basis of a combination of both. With the fused reaction products obtained at  $600^\circ C$ , it is difficult to resolve the problem by analytical methods. Using small quantities of depolarizer and long discharge times,

however, it was found that a greater than two-electron change was involved. On the basis of the weights of the reactants and the number of coulombs of energy obtained, the reduction corresponded to 3.8-electron change. However, the mix cake could not be analyzed for any unreacted depolarizer although attempts, including infra-red analysis were made. One may conclude, therefore, that a considerable part, if not all, of the energy is derived from the sulfate reduction. Since the total stoichiometry could not be established, one cannot demonstrate from this experiment that any energy was derived from the reduction of the copper ion, although particles of metallic copper were observed in the residues.

#### Package Design

A preliminary design study for a container for the high-power density battery has been started. One cell embodying some of the above design concepts has been assembled and tested. While it has been indicated that a leak-tight cell is possible to build and operate at 1100° F for 12 minutes, it will still be necessary to establish the following:

1. Maximum time the seals will endure the stresses at the elevated temperatures.
2. Substitute materials that can be used in place of those used in the above test.
3. Most economical design to give the greatest power density per cubic inch volume.
4. Materials balance for the most efficient electrochemical system.
5. Separator design to ensure complete separation of anode from cathode when extremely thin cells are assembled.
6. Number of heating and cooling cycles that cell can withstand before discharge.

The above problems are those contemplated for analysis in the immediate future.

The design of the first hermetically-sealed container, as shown in Figures 2, 3 and 4, consisted of the following:

1) Beryllium oxide has been selected as the spacer material between the current collectors. Beryllia has the greatest coefficient of thermal expansion and thermal conductivity of the ceramics investigated. Beryllia is considered safe in industrial applications where the operating temperatures are below 3200°F.

The faces of the beryllia ring are coated with molybdanese alloy, and this face, in turn, is nickel plated. Silver solder will stick to the nickel plating but not to the molybdanese coating.

2) The current collectors and nickel rings are vacuum brazed to the surface of the beryllia ring as shown in the arrangement in Figure 2 or 4.

3) The container is filled with the battery materials and a current collector is laid onto the face of the nickel ring and joined to it by welding. (See Figure 3.)

Theoretically, it should be possible to seal shut the container by either seam welding, "Heliarc" welding, or electron-beam welding. Tooling and welding techniques for the "Heliarc" welding in this application were developed by Union Carbide Parma Research Center Apparatus Shop.

This package design was reduced to practice on February 21, 1962, with the illustrated components.

#### Work Scheduled for Next Quarter

During the next quarter, the diffusion coefficient of the sulfate ion will be measured. If a solvent can be found for the phosphate ion, its diffusion coefficient will also be determined. In any event, the self-diffusion coefficient of this ion will be measured.

Also, during the next quarter, the cell work will involve additional investigation of phosphates and sulfates both as depolarizers and electrolytes. Preliminary work on balanced cells (little, if any, excess of either anode or depolarizer), particularly in sealed cell types of construction will continue.

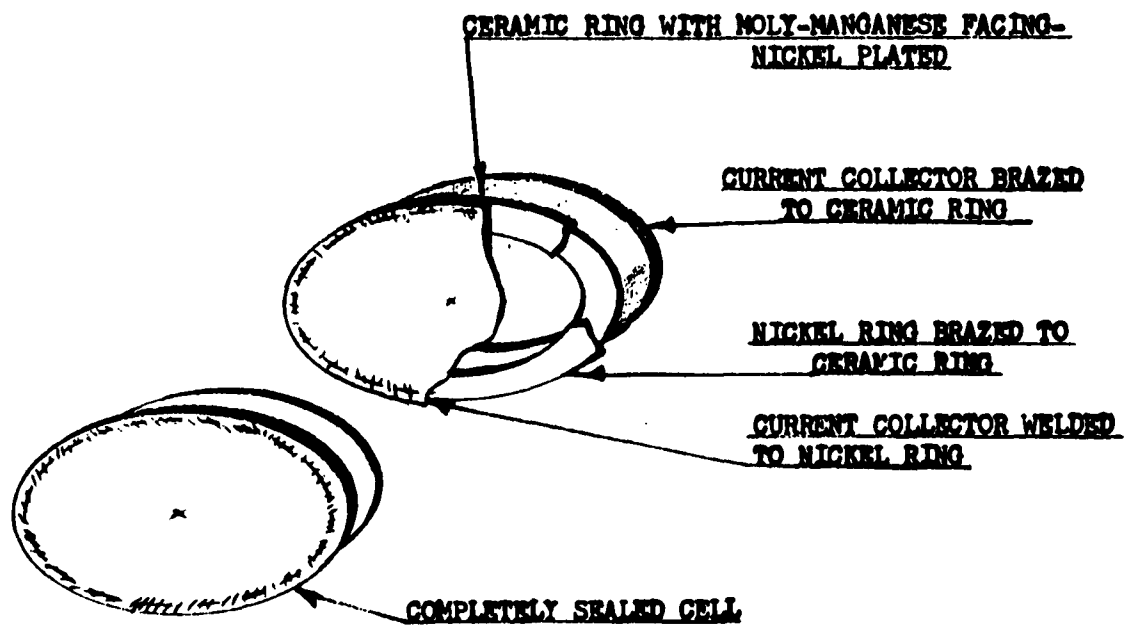
jdh

*T. J. Kutzweil*  
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FIGURE 2

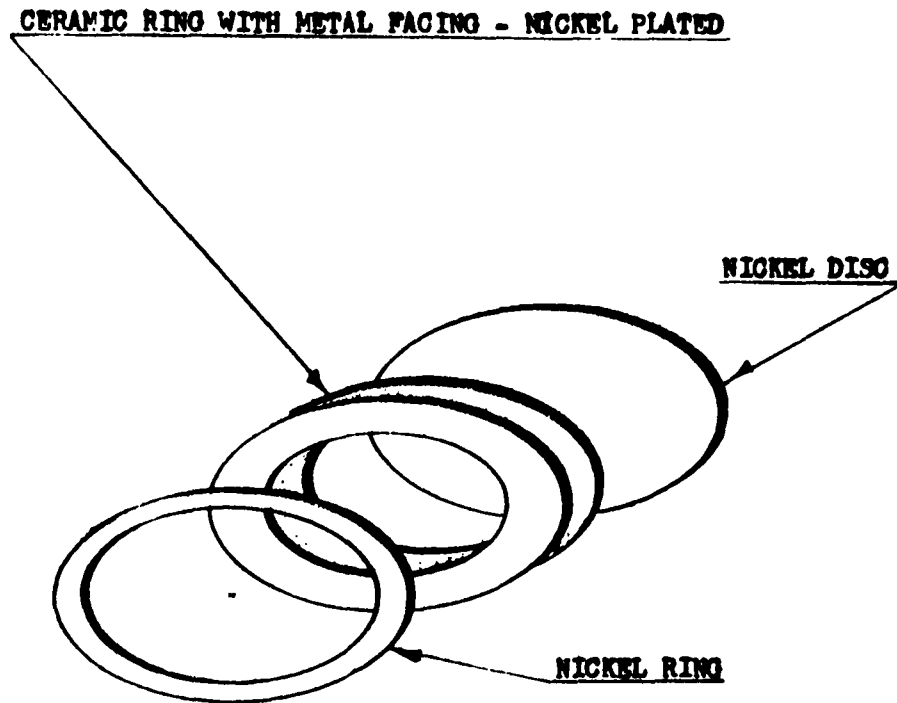
TENTATIVE DESIGN ARRANGEMENT OF  
OF COMPONENT PARTS FOR BATTERY CONTAINER



First reduced to practice 2/21/62

FIGURE 3

TENTATIVE DESIGN OF CONTAINER FOR  
THERMALLY ACTIVATED BATTERY



CERAMIC RING AND NICKEL RING AND NICKEL DISC TO BE ARRANGED AS SHOWN ABOVE  
AND BRAZED TOGETHER.

CENTER LINE OF NICKEL RING AND DISC TO BE CONCENTRIC WITH CENTER LINE OF CERAMIC  
RING WITHIN  $\pm .005"$ .

FIGURE 4

THERMALLY ACTIVATED BATTERY



C-1088

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