N87-11077

Presented at "The 1985 Goddard Space Flight Center Battery Workshop", Nov 1985.

DETERMINING THE INFLUENCE AND EFFECTS OF MANUFACTURING VARIABLES ON SULFUR DIOXIDE CELLS

W. V. Zajac, M. A. Thomas, J. A. Barnes, R. F. Bis,
P. B. Davis, F. C. DeBold, G.W. Gemmill, L. A. Kowalchik

Naval Surface Weapons Center
Silver Spring, Maryland 20903-5000

ABSTRACT

A survey of the Li/SO_2 manufacturing community was conducted to determine where variability exists in processing. The upper and lower limits of these processing variables might, by themselves or by interacting with other variables, influence safety, performance and reliability. A number of important variables were identified and a comprehensive design experiment is being proposed to make the proper determinations.

INTRODUCTION

The Lithium Systems Safety Group at the Naval Surface Weapons Center (NSWC) routinely evaluates lithium power sources for use in Naval applications. Also, in the course of accomplishing this mission and in order to keep abreast of new technology, members of the group actively participate in many research and development programs involving lithium systems. Although many lithium systems are being used and proposed for Naval applications, the Li/SO_2 cell is currently the most widely used and is expected to remain so for at least a decade.

The purpose of this work is to expand the current knowledge about Li/SO_2 cell fabrication which will result in even greater Naval confidence, wider acceptance, and use of this important power source. It is also felt that the information gained in this program will benefit the development and expanded use of other lithium systems as well.

BACKGROUND

A major problem that restricts greater use of Li/SO_2 cells is the lack of standardization among manufacturers and the uncertainty that exists when systems demand energy from these cells outside the regions where they have been previously tested. The regions of safe and reliable use are not just limited to performance capabilities, but performance as a function of environmental and mechanical stress factors such as time (storage) temperature and shock and vibration characteristic of Naval use.

The usual mode of acceptance testing involves simulated worst case evaluations on complete systems and pass/fail judgement can become subjective. In order to maximize confidence, all systems that undergo evaluation must remain static once approved for fleet use. Even with these safeguards, the Lithium Systems Safety Group occasionally receives disturbing safety or performance information from the scientific community suggesting that something might be different from previously tested and well characterized systems. Tracking down or trying to pinpoint causes for anomalous behavior can be very frustrating because reproducibility is often difficult and is compounded by our limited understanding of the complex chemistry and how it may interplay with unknown or proprietary fabricating techniques.

It was finally decided that in order to gain a full understanding of this system, special cells would need to be fabricated and tested. On the surface, this would appear to be a simple and straightforward task. However, due to the not so obvious subtleties of possible interactions between different variables, and also the fact that what might constitute a defect in one mode of operation might not necessarily be a defect in another, an appreciation for the complexity of this task begins to become apparent.

The need for an organized and unified experiment dictates that the experiment be designed in the classical sense using the powerful techniques referred to collectively as "statistical design of experiment". The rationale for this is simply that whenever the response from an experiment is associated with many variables and/or is subject to appreciable experimental variation, a statistically designed experiment offers the only sound and logical means of drawing valid conclusions. There is no question of any alternative which is equally satisfactory in economy or integrity.

The use of the above approach will require the efforts of statisticians with training and experience in the design and analysis of experiments. But, cooperative efforts in science are not new. Most research problems today have sufficient complexity that many disciplines and fields of specialization can contribute significantly to their solutions. This is certainly true in the area of lithium battery technology where the interdisciplinary efforts of battery scientists and statisticians have the best chance of resolving unanswered questions and uncovering unexpected results. NSWC is one of the few Navy laboratories which has a staff of statisticians available for consulting and analysis. Members of the statistics staff have been associated with the lithium battery problems in the past and have been instrumental in preparing the proposed design of experiment. The library of computer programs maintained by NSWC's staff was utilized in this preparation, and will be invaluable in the analysis of results after the conduct of the experiment.

EXPERIMENTAL DESCRIPTION

The experiment involves eleven compositional variables (referred to as factors) such as the type of carbon in the cathode and the electrolyte dryness. These factors will be considered at two levels each, i.e., two kinds of carbon, two electrolyte drynesses, etc. If it were known that there were no interactions among these factors, the experiment could be conducted on a reasonably small scale. However, since it is believed that the manufacture of safe Li/SO_2 batteries involves the interaction of variables, the experimental design must provide for the calculation of the interaction effects. Here, we define an interaction as a measure of the extent to which the effect (upon battery response) of changing one factor depends on the level of another.

This would be referred to as a two-factor (or first order) interaction. One can analogously define higher order interactions involving more than three factors. However, interactions higher than three-factor interactions are very difficult to interpret. It is generally believed that the interactions involved with the manufacture of Li/SO_2 batteries are not higher than first order (two-factor interactions). Therefore, a minimum design requirement is to provide for the calculation of all two-factor interaction effects. With eleven factors, there are 55 two-factor interactions. One approach to calculating their effects is to conduct an independent experiment with each of the 55 pairs of factors. Each experiment would require two levels of each factor represented in a 2 X 2 table of four different cell configurations. Hence, to proceed in this fashion, one would have to construct 4 X 55 = 220 cells. This would provide measures of the eleven main effects and 55 two-factor interactions. However, it would require 220 different cell configurations and for each response variable one should have at least five "identical" cells of each configuration to measure experimental variation. This is a total of 220 X 5 replicates = 1100 cells per response variable.

One can vastly improve upon the above scheme by employing the powerful technique of fractional factorial experimentation. To employ this technique with eleven factors at two levels each, we consider the 2^{11} = 2048 different cell combinations formed by crossing each two level factor, for example, see Figure I. However, a 2^{11} experiment would be both wasteful and unrealistic. It would provide information on main effects and two-factor interactions but also on all the other higher order interactions. These high order interactions can be assumed to be negligible, and it is, therefore, not necessary to measure them. One can sacrifice their information by performing only a "fraction" of the full 2^{11} factorial experiment. The degree of fractionation depends upon which interactions one is willing to sacrifice information. Using the previously stated belief that one need not be concerned with interactions beyond first order (two-factor), we need only perform a one-sixteenth fraction of a 2^{11} factorial. This requires 128 different cell configurations (vice the earlier figure of 220). Also, in this design, each two-way interaction is measured with an effective cell replication of 32 (vice the earlier figure of 5). If we allow two replicates per response variable to provide measures of variation in each of the 128 experimental cells, the cost would be 128 X 2 replicates = 256 cells per response variable (vice the earlier figure of 1100). This is a reduction in cost by more than a factor of four. In addition, each main effect and two-factor interaction is measured with much greater precision than before. Also, all information on higher order interactions is not lost. While much has been sacrificed by fractionation, there will still be clean measurements of many three-factor interactions. Hence, by employing "design of experiment" techniques, we actually gain precision and also gain information on some high order interactions with less than one fourth the number of batteries required by treating the experimental process as 55 independent experiments.

VARIABLES

After extensive discussions with all the major Li/SO_2 manufacturers concerning this project, all identifiable variables were grouped into three basic categories: (1) compositional, (2) geometric, and (3) design/process.

Compositional variables refer to major cell components and their purity levels and are universal or common to all cell designs. It is because of this commonality that compositional variables were selected for this study. Geometric and design variables refer to such things as thickness of cathode, vent type, use of anodic current collectors, etc. However, although geometric and design variables are important, it was felt that a strong foundation based upon compositional variables would need to be established before proceeding with a determination of the effects of non-compositional variables. Some examples of geometric and design variables are given in Figure II.

A listing of the eleven compositional variables, each identified alphabetically, can be correlated with the experimental outline (Figure I) showing a one-sixteenth replicate of a 2^{11} factorial experimental design.

A. Carbon Type
B. Carbon Purity
C. Teflon Type
D. Cathode Dryness
E. Sodium in Anode
F. Nitrogen in Anode
G. Passivation of Anode
H. Lithium Bromide Purity
J. Electrolyte Dryness
K. Acetonitrile Purity
L. SO_2: Lithium (Ratio)

An in depth discussion on the relative merits of the selected compositional variables including the proposed two levels for each variable would be too lengthy for this paper. However, they will be discussed in some detail at the oral presentation, time permitting.

MEASUREMENTS AND RESPONSES

Although the Lithium Sulfur Dioxide chemistry is firmly established as a valuable power source for certain Naval applications, NAVSEA NOTE 9310 still mandates that all systems utilizing lithium must be approved for safety prior to use in the fleet. The four basic NAVSEA NOTE 9310 test protocols of forced overdischarge, charge, short circuit and heat tape will form the backbone of the measurement scheme. Preconditioning of cells, i.e., mechanical shock, diurnal and long term storage is planned. A full spectrum of discharge conditions at various rates and temperatures will be made.

Surface responses that will be correlated with the compositional variables will be capacity, power, voltage delay, thermal behavior and time (Δt) to an event (explosion or venting). Several test matrixes are being considered with the emphasis on obtaining maximum information and efficiency. It is currently felt that less than 50 cells at each of the 128 experimental conditions should be more than satisfactory to accomplish this task.

CONCLUSION

There is no question that the project outlined in this paper is an ambitious one. We also feel that a successfully completed project will have no null result because what is really being pursued is the elimination of uncertainty. Furthermore, we strongly believe that valuable clues leading to improvements in other higher energy density lithium systems will be gleaned.

Finally, after many discussions with members of our staff at NSWC, it was decided that the information gained from our survey leading to the development of this design experiment was an important end itself and worthy of presentation to the lithium battery community which would hopefully be appreciative and become stimulated to pursue these and other ideas in a similar fashion on their own.

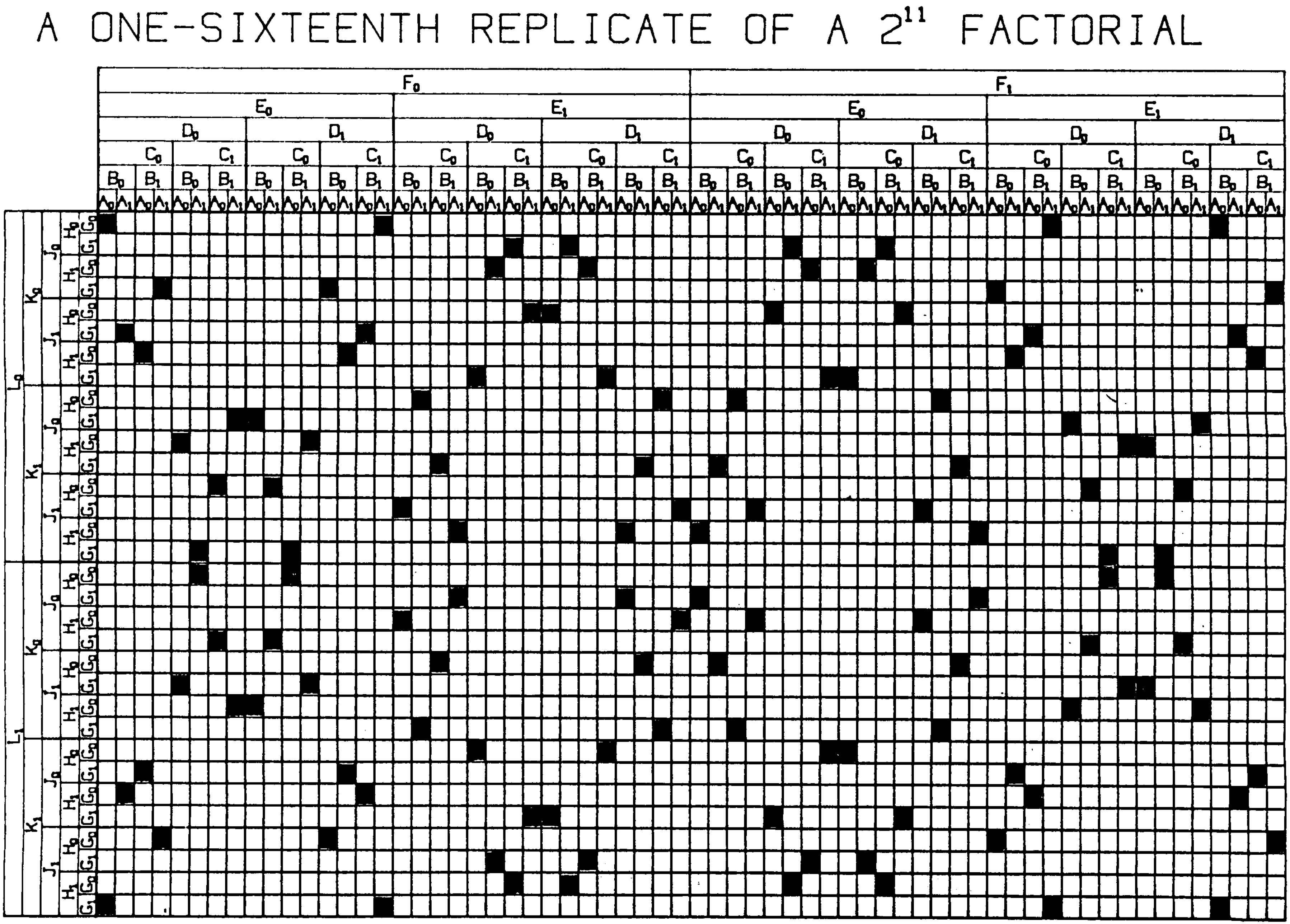

Figure 1. A ONE-SIXTEENTH REPLICATE OF A 2^{11} FACTORIAL

COMPOSITIONAL	GEOMETRIC	DESIGN/PROCESS
CARBON TYPE	VOID VOLUME	GLASS TO METAL SEAL
CARBON PURIFICATION STEP.	TIGHTNESS OF WRAP CONCENTRICITY OF WRAP	CURRENT COLLECTOR TYPE
TEFLON TYPE		TABBED VS. COLD WELDED
CATHODE DRYNESS	REGISTERING	STAINLESS VS. NICKEL PLATED IRON
SODIUM IN ANODE	SEPARATOR THICKNESS	VENT TYPE
NITROGEN IN ANODE	ANODE THICKNESS	CATHODE PROCESSING TECHNIQUES
PASSIVATION OF ANODE	CATHODE THICKNESS	
AN PURITY	MESH GEOMETRY	
ELECTROLYTE DRYNESS		
SO_2:Li		
LiBr PURITY		

Figure 2. EXAMPLES OF VARIABLES