

Prismatic thionyl chloride cell characterization through parametric analysis

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Received 1 March 1994; accepted in revised form 6 June 1994

Abstract

The Taguchi method of experimental design was followed to investigate and understand the performance and general electrical characteristics of prismatic lithium/thionyl chloride cells as functions of electrolyte salt, electrolyte salt concentration, anode pre-treatment, and exposure to elevated temperature. An L8 matrix was used to assess the effects of each of the 4 independent variables on open- and closed-circuit voltages, capacity under discharge, cell thickness, internal impedance, and heat dissipation. ANOVA analysis of the 48 cell population has allowed the projection of optimized prismatic lithium/thionyl chloride cells, through the use of 0.5 M lithium tetrachloroaluminate in thionyl chloride as the catholyte. The salt concentration was found to have the greatest impact on cell performance in terms of delivered capacity.

Keywords: Thionyl chloride cells; Parametric analysis

1. Introduction

Experimental design has been used in a variety of applications in industrial settings, and has proven to be of value in virtually all engineering fields and business applications [1]. The main advantages of the technique, according to Barker [2], are fourfold, as the process allows for a structured plan of attack, increased efficiency, the use of powerful analysis tools, and requires an organized experimenter. Three major approaches to experimental design are generally discussed. These are the foundations described by Taguchi [3], Shainin [4], and Deming [5].

The underlying goals of experimental design are to improve productivity and efficiency when conducting experiments to identify important variables which significantly contribute to the overall variation in a designated output. By using a well-defined structure to simultaneously study the impact of several variables on the desired output, positive (additive) and negative (parasitic) interactions can be discerned from a small number of data sets. As an extension of the *t*-test, analysis of variance (ANOVA) is typically used for data evaluation to determine if statistically significant differences exist among the means of several test pop-

ulations, each thought to follow a normal distribution. The ANOVA technique may be used to identify, simultaneously, the effect of several independent variables on a given dependent variable.

This type of approach to design optimization is well-suited for battery development, especially when the cost incurred per test vehicle may be significant. One such example is the development of lithium/thionyl chloride (Li/SOCl₂) cells. A characteristic of lithium/liquid oxidant cells is that units exposed to elevated temperatures typically deliver less capacity than cells which have not undergone any heat treatment [6]. Also, capacity losses due to self-discharge must be considered when attempting to optimize a product, especially one used in implantable applications [7].

In order to improve the discharge characteristics and/or performance of Li/SOCl₂ cells, the areas of opportunity include the catholyte, specifically, the lithium salt added to increase the conductivity of the thionyl chloride, as well as the final concentration of that salt, and anode pre-treatment. Described herein is an application of the Taguchi approach to experimental design in the characterization of a prismatic Li/SOCl₂ cell product.

2. Experimental

2.1. Cell construction

Prismatic, hermetically sealed, case-positive cells measuring 8.6 mm × 22.8 mm × 45.0 mm were used as test vehicles. Anodes were fabricated using 99.8% pure lithium obtained from Cyprus Foote Mineral Company, by pressing pre-cut blanks to each side of a nickel screen equipped with leads. The lithium was then pre-treated using one of two proprietary treatments, hereafter referred to as pre-treatment 1 or 2. The anode assemblies were wrapped in a glass fiber separator (Mead Paper, Specialty Paper Division), then enveloped in a Zitex (Norton) separator, and positioned between two carbon plates composed of Shawinigan Black and polytetrafluoroethylene pressed onto stainless-steel grids.

The catholyte consisted of either 0.5 or 1.5 M lithium tetrachloroaluminate (LAC) or lithium tetrachlorogallate (LGC) in thionyl chloride. Lithium chloride was dried under vacuum for a minimum of 16 h at 120 °C, followed by additional drying at 260 to 300 °C for another 16 h before use. The aluminum and gallium trichloride salts, as well as the thionyl chloride, were used as received. Heat-treated cells were subjected to two, 60 min autoclave simulation cycles at 130 ± 5 °C. The cells were allowed to equilibrate to room temperature prior to the application of the second heat cycle. During this equilibration, cell thickness was recorded. Six cells were constructed to represent each set of conditions designated by the L8-2-7 matrix, yielding a total cell population of 48 cells.

2.2. Cell testing

All cells were pre-discharged at 37 °C by placement under a 1 kΩ resistive load for 15 min. Following a 21-day open-circuit storage period at 37 °C, the cells were discharged under 2 kΩ loads at 37 °C. Open-circuit voltage (OCV), closed-circuit voltage (CCV), and internal impedance readings measured at a frequency of 1 kHz, were recorded using an in-house, semi-automatic measuring system interfaced with a Prime computer. The heat dissipation of the cells was recorded at room temperature using a Tronac calorimeter (Model 351RA). The cells were taken off-load a minimum of 3 days prior to the heat dissipation measurement and remained on open circuit during the measurement.

ANOVA was conducted using Lab Partner Design of Experiments® software (Sof-Ware Tools, Version 1.5, Boise, ID, 1990).

3. Results and discussion

The successful use of experimental design first requires the identification of the best matrix for the study of the independent variables. Full or fractional factorial arrays may be employed. The Taguchi approach has developed 18 standard orthogonal arrays which may be used to analyze up to 31 independent variables at 1 to 4 levels. Included in the 18 standard arrays are some mixed level matrices which allow for the examination of several variables at various levels. The standard line graphs of the 18 arrays allow identification of the best matrix and planning the necessary experiments, as placement of the independent variables under study into the matrix is critical to the interpretation of the ANOVA results. Therefore, choice of array and placement of variables into the matrix are important considerations for full utilization of the experimental design approach.

In this investigation of 4 independent variables, each at 2 levels, the fractional factorial L8-2-7 matrix was chosen as the working array. The matrix moniker indicates that 7 variables, each at 2 levels, settings, or conditions, may be analyzed, as shown in Fig. 1(a). However, because of interactions of the variables as depicted in the line diagram of Fig. 1(b), the matrix was used to study the effects of 4 variables, each at 2 levels. The selections for each of the 4 variables under investigation were chosen as: (i) electrolyte salt (lithium tetrachloroaluminate or lithium tetrachlorogallate); (ii) salt molarity (0.5 or 1.5 M in thionyl chloride); (iii) heat treatment (autoclaved or not heat-treated), and (iv) anode pre-treatment (1 or 2). Within the L8-2-7 matrix, as shown in Fig. 1(b), interactions occur between the variables placed in columns 1 and

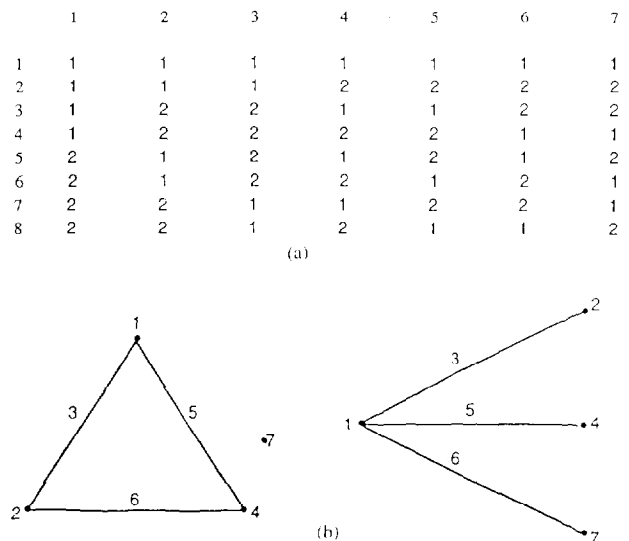


Fig. 1. (a) Standard Taguchi L8-2-7 matrix; (b) Line diagrams of standard Taguchi L8-2-7 matrix.

2, with the interaction being manifest in column 3. Similar interactions occur between the independent variables placed in columns 1 and 4, and those between columns 2 and 4, with the interactions becoming manifest in columns 5 and 6, respectively. For the variable placed in column 7, interactions with the other 3 variables cannot be studied directly. Therefore, the independent variables were placed into the matrix as follows: column 1–electrolyte salt; column 2–anode pre-treatment; column 3–interaction of electrolyte salt and anode pre-treatment; column 4–heat treatment; column 5–interaction of electrolyte salt and heat treatment; column 6–interaction of anode pre-treatment and heat treatment, and column 7–molarity, as depicted in Table 1.

There were several outputs of interest: OCV, capacity under discharge, cell thickness at end-of-life, internal impedance, heat dissipation, and CCV. The contributions of the independent factors upon the variability of each dependent variable, or output, were analyzed separately.

Table 2 lists the average 21 day OCV of each cell group. It can be seen that the conditions of 1.5 M LAC, anode pre-treatment 1, and no heat treatment gave the highest open-circuit potentials (group 3). Using the quality condition of ‘the bigger the better’ to describe the OCVs (i.e., higher voltages are desirable over low 21-day OCV readings), it can be seen in Table 3 that the only independent variable, which contributed significantly to this output, was the lithium salt (43.66%). An important interaction was also found between the lithium salt and the anode pre-treatment used (23.74%). The ‘main effects analysis’ of the Lab Partner[®] program (Table 3), which lists the optimum settings to employ in order to achieve the desired quality of the output, confirmed that group 3 conditions were the best for realizing high 21-day OCVs.

Capacity delivered upon discharge to a 3 V cutoff was subsequently analyzed. Fig. 2(a) contains a typical

discharge profile of a non-heat-treated cell, while Fig. 2(b) illustrates a typical discharge profile of a heat-treated unit. A summary of the average capacities (± 1 SD) delivered to 3 V by the 8 cell groups is presented in Table 4. As shown in Table 3, molarity was identified, at a 99.5% confidence level, as the most important factor contributing to the variation in capacity. Also, the interaction of salt and heat, the interaction of salt and anode pre-treatment, and the choice of lithium salt were identified as having contributions greater than that of the residual error. According to these data, the greatest capacity (quality characteristic ‘the bigger the better’) to a 3 V cutoff should be delivered by non-heat-treated, prismatic cells filled with 0.5 M LAC in thionyl chloride utilizing anode pre-treatment 1.

The impacts of each of the 4 variables and their interactions upon cell thickness recorded at end-of-life (EOL) under the 2K discharge test are also listed in Table 3. Using the quality characteristic of ‘the smaller the better’ to describe the desired output of least cell swelling (less thickness increase due to autoclave and/or discharge), heat treatment was identified to be the most important variable. When exposed to elevated temperature, the thermal expansion of liquid SOCl_2 causes cell swelling. In addition, the thermal decomposition of SOCl_2 into S_2Cl_2 , SO_2 , and Cl_2 [8] may also account for some of the increase in cell thickness upon autoclave. During cell discharge, the generation of SO_2 (gas), through the reduction of thionyl chloride, also contributes to the increase in cell thickness. Although neither the lithium salt nor the anode pre-treatment was found to contribute significantly to EOL thickness, their interaction was found to contribute almost 20% to the output. In addition, catholyte salt molarity was found to give almost a 13% contribution to EOL thickness when the data were analyzed using

Table 1
Description of experiment

Title of experiment: prismatic SOCl_2 cell characterization through parametric analysis.
Goal/objective: cell optimization/performance study.
Procedure: 8.6 mm prismatics.
Standard orthogonal array model used: L8-2-7.

| Column | Label | Description of factor | Level 1 | Level 2 | Level 3 | Level 4 |
|--------|-------|-----------------------|------------------|------------------|---------|---------|
| 1 | S | Salt | LAC ^a | LGC ^b | | |
| 2 | A | Anode pre-treatment | 1 | 2 | | |
| 3 | SXA | | 1 | 2 | | |
| 4 | H | Heat treatment | No | Yes | | |
| 5 | SXH | | 1 | 4 | | |
| 6 | AXH | | 2 | 4 | | |
| 7 | M | Molarity | 0.5 | 1.5 | | |

^aLAC: lithium tetrachloroaluminate.

^bLGC: lithium tetrachlorogallate.

Table 2
Twenty-one day open-circuit voltages

| Group description | Average OCV (mV) |
|---|------------------|
| 1. 0.5 M LAC ^a , anode pre-treatment 1, non-heat-treated | 3679.50 ± 2.59 |
| 2. 1.5 M LAC, anode pre-treatment 1, heat-treated | 3681.33 ± 2.16 |
| 3. 1.5 M LAC, anode pre-treatment 2, non-heat-treated | 3740.67 ± 8.14 |
| 4. 0.5 M LAC, anode pre-treatment 2, heat-treated | 3694.50 ± 3.39 |
| 5. 1.5 M LGC ^b , anode pre-treatment 1, non-heat-treated | 3663.83 ± 7.08 |
| 6. 0.5 M LGC, anode pre-treatment 1, heat-treated | 3679.17 ± 6.01 |
| 7. 0.5 M LGC, anode pre-treatment 2, non-heat-treated | 3653.17 ± 1.94 |
| 8. 1.5 M LGC, anode pre-treatment 2, heat-treated | 3663.67 ± 6.80 |

^aLAC: lithium tetrachloroaluminate.

^bLGC: lithium tetrachlorogallate.

Table 3
Summary of ANOVA analyses

| Output | 21-day OCV | Capacity to 3 V | EOL thickness | Impedance at 3 V | Heat dissipation at BOL | Heat dissipation at mid-life | Running voltage |
|---------------------------|--------------------|--------------------|--------------------|--------------------|-------------------------|------------------------------|-----------------|
| Quality characteristic | Bigger | Bigger | Smaller | Smaller | Smaller | Smaller | Bigger |
| Analysis of variation (%) | | | | | | | |
| Factor | | | | | | | |
| Salt (S) | 43.66 ^a | 3.77 ^a | 0.48 ^a | 1.75 ^b | 31.33 ^a | 19.98 ^a | 7.83 |
| Anode pre-treatment (A) | 5.38 ^a | 0.46 ^b | 0 | 15.31 ^a | 0 | 5.58 ^a | 70.43 |
| Interaction SXA | 23.74 ^a | 3.92 ^a | 19.67 ^a | 5.05 ^a | 0 | 1.37 ^b | 0.87 |
| Heat treatment (H) | 0.72 ^a | 0 | 65.04 ^a | 0 | 22.23 ^a | 0.76 | 0 |
| Interaction SXH | 11.53 ^a | 4.81 ^a | 0.51 ^a | 49.4 ^a | 30.48 ^a | 0 | 3.48 |
| Interaction AXH | 6.5 ^a | 1.06 ^a | 0.03 | 2.5 ^a | 0 | 20.43 ^a | 13.91 |
| Salt molarity (M) | 4.31 ^a | 82.27 ^a | 12.99 ^a | 12.63 ^a | 6.16 ^b | 48.93 ^a | 3.48 |
| Error | 4.17 | 3.71 | 1.27 | 13.37 | 9.79 | 2.95 | 0 |

^a99.5% confidence.

^b95% confidence.

Main effects (optimum settings)

| Factor | LAC ^a | LAC | LGC ^b | LAC | LAC | LGC | LAC |
|---------------------|------------------|-----|------------------|-----|-----|-----|-----|
| Salt | LAC ^a | LAC | LGC ^b | LAC | LAC | LGC | LAC |
| Anode pre-treatment | 2 | 1 | 2 | 2 | 2 | 2 | 1 |
| Heat treatment | No | No | No | No | Yes | Yes | Yes |
| Salt molarity | 1.5 | 0.5 | 1.5 | 0.5 | 0.5 | 0.5 | 1.5 |

^aLAC: lithium tetrachloroaluminate.

^bLGC: lithium tetrachlorogallate.

the Lab Partner[®] program. As the density of the electrolyte increased as a function of increased salt concentration, less thionyl chloride solvent was available for reduction. This resulted in reduced cell performance, as well as reduced cell swelling of units filled with either 1.5 M LAC or LGC in thionyl chloride. It should be mentioned that the smaller the value attributed to *e*, the residual error associated with each ANOVA analysis, the more completely the variation in output has been described by the variables under study. In this analysis, the residual error accounted for 1.27% of the overall variation in cell thickness, indicating that the 4 chosen variables and their interactions were appropriate to understanding the major contributions to cell swelling.

The influence of the 4 independent variables upon the internal cell impedance recorded during discharge was investigated. Examples of internal impedance plotted as a function of delivered capacity of non-heat-treated and heat-treated cells are shown in Fig. 2(a) and (b), respectively. A summary of the average internal impedances of the 48 cells recorded at a cutoff of 3 V is found in Table 4. This output is a consideration when optimizing cell designs, as impedance may be used as an indicator for elective replacement of the power source. Additionally, it is necessary that the impedance of the power source not rise to a level which would effectively shut down operation of the device. At a potential of 3 V, cell impedance was found to be mainly governed by the interaction of the choice of lithium salt and heat treatment, and by the anode

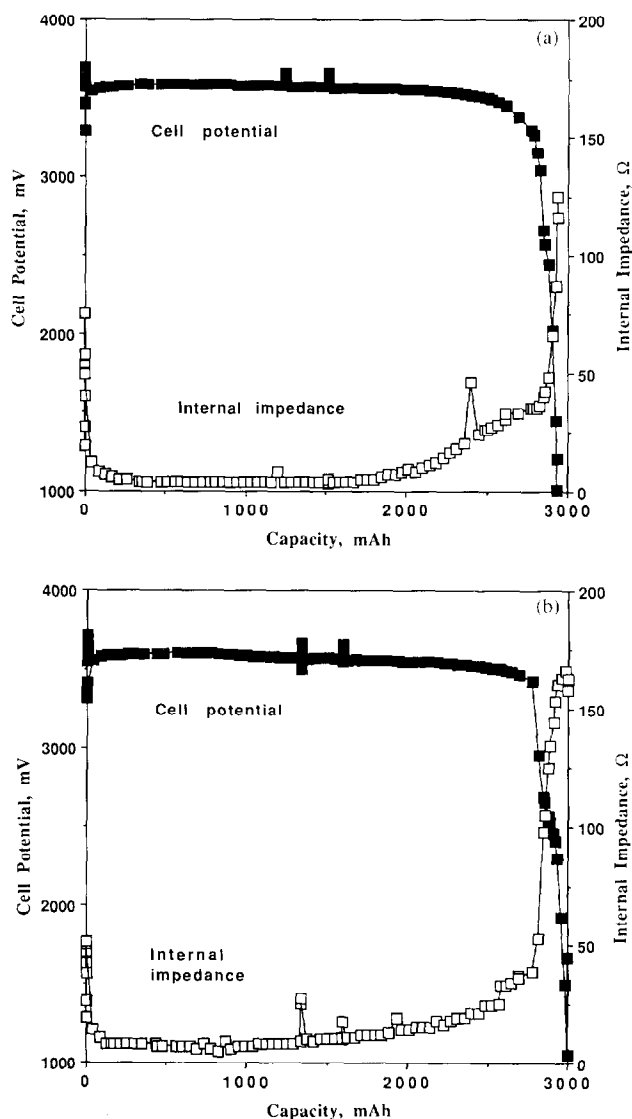


Fig. 2. (a) Profile of non-heat-treated cell discharged under 2 k Ω load at 37 $^{\circ}$ C, group 1, 0.5 M lithium tetrachloroaluminate, anode pre-treatment 1. (b) Profile of heat-treated cell discharged under 2 k Ω load at 37 $^{\circ}$ C, group 6, 0.5 M lithium tetrachlorogallate, anode pre-treatment 1.

pre-treatment (Table 3). Using the quality characteristic of 'the smaller the better', the optimum settings for the 4 variables were found to be 0.5 M LAC, pre-treatment 2, and no heat treatment (Table 3).

Heat dissipation, or the measure of self-discharge, may also be of interest as side reactions may occur between active components, especially after exposure to elevated temperatures. Since power sources for implantable devices are typically under only micro- or milliampere drain rates [7], losses of capacity due to parasitic cell reactions could cause the unit to reach EOL prematurely. The heat dissipation of 2 cells per each of the 8 test groups was measured twice during this study; once at the beginning-of-life (BOL) prior to placement under discharge loads, and again at ap-

Table 4

Average capacities delivered and internal impedances recorded at 3 V

| Cell group designation | Capacity (mAh) | Internal impedance (Ω) |
|------------------------|----------------|---------------------------------|
| 1 | 2740 \pm 58 | 33 \pm 8 |
| 2 | 2131 \pm 53 | 327 \pm 51 |
| 3 | 2341 \pm 22 | 10 \pm 4 |
| 4 | 2681 \pm 95 | 61 \pm 8 |
| 5 | 2073 \pm 91 | 258 \pm 102 |
| 6 | 2802 \pm 34 | 61 \pm 23 |
| 7 | 2512 \pm 30 | 176 \pm 27 |
| 8 | 2039 \pm 34 | 68 \pm 15 |

Group 1:

0.5 M LAC^a, anode pre-treatment 1, non-heat-treated

Group 2:

1.5 M LAC, anode pre-treatment 1, heat-treated

Group 3:

1.5 M LAC, anode pre-treatment 2, non-heat-treated

Group 4:

0.5 M LAC, anode pre-treatment 2, heat-treated

Group 5:

1.5 M LGC^b, anode pre-treatment 1, non-heat-treated

Group 6:

0.5 M LGC, anode pre-treatment 1, heat-treated

Group 7:

0.5 M LGC, anode pre-treatment 2, non-heat-treated

Group 8:

1.5 M LGC, anode pre-treatment 2, heat-treated

^aLAC: lithium tetrachloroaluminate.

^bLGC: lithium tetrachlorogallate.

proximately 50% depth-of-discharge. ANOVA analysis of the microcalorimetry results identified the lithium salt, heat treatment, and their interaction as the top 3 contributors to low BOL heat dissipation, as shown in Table 3. Near mid-life, salt molarity, the choice of lithium salt, the interaction between heat treatment and anode pre-treatment, as well as the choice of anode pre-treatment were found to be the major factors contributing to low heat dissipation (Table 3). The optimum settings for low BOL heat dissipation are the use of 0.5 M LAC in SOCl₂ catholyte in non-heat-treated cells utilizing anode pre-treatment 2, while at mid-life, heat-treated cells filled with 0.5 M LGC in SOCl₂ using anode pre-treatment 2 should dissipate the least amount of heat.

In order to design a prismatic Li/SOCl₂ cell optimum for several implantable applications, reasonably high open-circuit and running voltages for efficient operation of the device circuitry, a low rate of self-discharge, low impedance during discharge, consistent delivery of the greatest achievable capacity, and minimal swelling upon discharge are desired characteristics.

From the 8 cell populations investigated, the discharge profiles indicated that to a 3 V cutoff, heat-treated cells filled with 0.5 M LGC in SOCl₂ catholyte and using anode pre-treatment 1 (group 6) delivered the

greatest capacity (2802 ± 34 mAh). This performance was found to be statistically better than that of non-heat-treated cells filled with 0.5 M LAC in SOCl_2 catholyte also using the pre-treatment 1 (2740 ± 58 mAh, Table 4, group 1) when the data were analyzed using the student's *t*-test (95% confidence). However, as summarized in Table 4, the average EOL internal impedance of group 6 cells was $61 \pm 23 \Omega$, while that of group 1 cells was statistically lower, being only $33 \pm 8 \Omega$.

From the discharge data, it may also be seen that the average capacity delivered to 3 V by group 1 cells (0.5 M LAC, non-heat-treated, anode pre-treatment 1) was not statistically higher than that of group 4 cells (0.5 M LAC, heat-treated, anode pre-treatment 2). Although cell impedance during discharge remained fairly low for each group, the average 1 kHz internal impedance of the non-heat-treated cell population was statistically lower. Therefore, it appears that 0.5 M LAC in SOCl_2 should be the catholyte of choice, as confirmed by the ANOVA analyses of delivered capacity. It also appears that autoclave treatment and anode pre-treatment had very little impact on cell discharge performance when 0.5 M LAC in SOCl_2 catholyte was used. Autoclaved cells have a larger BOL cell thickness than non-heat-treated cells, but tend to swell less upon discharge (ANOVA analysis of EOL cell thickness).

Low BOL and mid-life heat dissipation were found when cells utilized anode pre-treatment 2, although its percent contribution to variation in heat dissipation was small in each ANOVA analysis of the micro-calorimetry results. Anode pre-treatment was, however, found to be the major contributor to the variation noted in running voltages. As listed in Table 3, it accounted for over 70% of the variation in running voltage. Anode pre-treatment 1 was identified by the 'main effects analysis' as being the optimum setting for high running voltage, along with the use of heat treatment and 1.5 M LAC in SOCl_2 catholyte. However, the use of 1.5 M salt solutions generally gives rise to higher internal impedance and lower delivered capacity, while heat treatment may cause increased cell swelling. Therefore, the characteristics of the most versatile prismatic Li/ SOCl_2 cell include the use of 0.5 M LAC in SOCl_2 as the catholyte. The choice of anode pre-treatment alone, most greatly influences impedance and running voltage, while its interactions with electrolyte salt and heat treatment contribute to variation in OCV and CCV, cell thickness, and mid-life heat dissipation. From

these results it appears that either pre-treatment may be used, with little effect on cell performance. However, the use of proprietary pre-treatment 2 may be preferred as it is identified as the optimum setting for 5 of the 7 outputs investigated. Heat treatment of cells built according to these specifications should have only a minimal effect upon discharge performance.

4. Conclusions

The advantages of the Taguchi approach are several. Time and effort are minimized when the influence of several independent variables upon various outputs of interest may be analyzed simultaneously. If this study would have been carried out using factor by factor analysis, 96 cells would have been needed. Utilization of the Taguchi approach reduced the number of necessary units by 50%. With 6 cells built according to each of the 8 sets of experimental conditions, the optimum lithium salt to be added to increase the conductivity of the thionyl chloride catholyte, its concentration, and the type of anode pre-treatment to be used were able to be determined when each variable was studied at 2 levels. The effect of heat treatment on cell OCV and CCV, swelling, discharge capacity, internal impedance, and heat dissipation were also investigated, as some medical devices may be sterilized by exposure to elevated temperatures prior to implantation. From the study, it was found that the catholyte salt concentration played the major role in influencing the variability in delivered capacity.

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