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Use of multiple regression analysis to develop equations for predicting Li–Al/iron sulphide cell performance

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A multiple regression analysis was conducted to develop predictive equations for the specific energy and specific power of Li–Al/iron sulphide cells over a wide range of cell designs and operating variables. The intent was to make these equations as general as possible such that one set of equations would predict the performance of Li–Al/FeS or Li–Al/FeS_2 cells with bicell (one positive electrode and two facing negative electrodes) or multiplate cell configurations. Data from 33 cells were used in the analysis of specific energy, and 26 cells were used to develop the specific power equation. The calculated specific energy and specific power showed good agreement with the measured values for these cells. In general, the deviation between the calculated and measured values was within ± 10%. A check of the predictive capability of these equations also showed good agreement. The specific energy and specific power calculated for 14 cells not used in the regression analysis deviated by ± 10% from the measured values. These equations were used to identify the most likely cell designs to meet selected electric-vehicle battery performance goals. These designs were included in an experimental programme for further performance evaluation.

Nomenclature

A_e	limiting electrode area (cm^2)
AHREFF	coulombic efficiency (%)
b_i	constants in multiple regression equation
CCO	cell charge cut-off voltage (V)
CF	charge factor (1.0 for fully charged cell, 0.5 for cell 50% discharged, 0.05 for cell discharged to a cut-off of 0.9–1.0 V)
DCO	cell discharge cut-off voltage (V)
FCCF	fully charged correction factor (1.0 for fully charged cell, 0.05 for any state of discharge)
FSLMUL	product of FSUBL and MUL (defined below)
FSUBL	calculated utilization factor of the limiting electrode (%)
i_c	charge current density ($A\,cm^{-2}$)
i_D	discharge current density ($A\,cm^{-2}$)
MUL	theoretical specific energy factor ($W\,h\,kg^{-1}$)
NSPTHC	negative-to-positive capacity ratio
OCV	cell open-circuit voltage (V)
OFFEUT	factor related to LiCl composition in electrolyte (%)
PF	power factor ($W\,kg^{-1}$)
POSPIN	reciprocal of the number of positive electrode plates
PPXCYC	product of the number of positive electrode plates in the cell and the number of deep discharge cycles
R^2	correlation coefficient
$\bar{R}_c$	average cell resistance (Ω)
SP	calculated cell specific power ($W\,kg^{-1}$)
SPECYC	calculated cell specific energy ($W\,h\,kg^{-1}$)
SPEBAS	calculated cell specific energy early in life ($W\,h\,kg^{-1}$)
TEMPR	temperature ratio
TSUBCR	thickness ratio of counter electrode and electrode separator
VFSNEG	volume fraction salt in the negative electrode
VFSPOS	volume fraction salt in the positive electrode

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VOLT1R	discharge voltage factor
VOLT2R	charge voltage factor
W	cell weight (kg)
X_i	independent variables in regression equation
$\hat{y}$	dependent variable in regression equation

1. Introduction

The lithium/iron sulphide battery development at Argonne National Laboratory (ANL) and ANL's industrial subcontractors is primarily concerned with the development of high-performance secondary batteries for electric-vehicle propulsion [1]. The major requirements for an electric-vehicle battery are high specific energy (W h kg^{-1}), high volumetric energy density (W h dm^{-3}) and high specific power (W kg^{-1}). Economic considerations require a minimum battery lifetime of about 3 years (about 1000 deep discharge cycles or equivalent) and an eventual cost of about \$50–60 kW^{-1} h^{-1}.† This paper describes an empirical technique, based on multiple regression analysis of cell performance data, that provides a means of determining optimum cell designs with respect to specific energy, cycle life and specific power. This technique can be expanded to allow for the determination of optimum designs with respect to cost.

The battery cells currently under development consist of a lithium–aluminium (Li–Al) negative electrode, an iron sulphide (FeS) positive electrode, a boron nitride (BN) felt separator to provide electrical isolation of the electrodes, and a molten LiCl–KCl electrolyte [2]. The melting point of the electrolyte (352° C at the eutectic composition of 58.2 mol% LiCl) requires a battery operating temperature in the range 400–500° C. The overall reaction products for the Li–Al/FeS cell are lithium sulphide (Li_2S), iron and aluminium. The theoretical specific energy for this cell based on the weights of the reactants and products is about 460 W h kg^{-1}, and the voltage versus capacity curve has a single voltage plateau at about 1.3 V. The electrochemical reaction is complex; for example, an intermediate compound $LiK_6Fe_{24}S_{26}Cl$ (J-phase) [3] is formed through a reaction with the KCl in the electrolyte.

During the past few years, the cells have been prismatic in shape and assembled with either one positive electrode and facing negative electrodes (bicell design) or two or more positive electrodes and facing negative electrodes (multiplate design). The electrode area was about 270 cm^2 (12.7 cm x 12.7 cm electrodes) for the bicells and 1800 cm^2 (17.8 cm x 17.8 cm electrodes) or 900 cm^2 (12.7 cm x 17.8 cm electrodes) for the multiplate cells. The electrodes were generally cold-pressed from powdered mixtures of active material and electrolyte. The remainder of the electrolyte was loaded into the cells by a vacuum technique.

Another lithium/iron sulphide cell system of interest, one that has received less development effort at ANL, is the Li–Al/FeS_2 cell. The theoretical specific energy, based on the weights of reactants and products, is about 650 W h kg^{-1} The voltage versus capacity curve has two voltage plateaus, one at about 1.7 V and the other at about 1.3 V. This cell system has received less development effort because of difficulty in finding a suitable low-cost metallic current collector [4, 5] and some problems with capacity loss during cycling [6].

The programme on the electric-vehicle battery involves the development, design and fabrication of a series of lithium/iron sulphide batteries, designated Mark IA, II and III. The Mark IA battery was fabricated in 1979. As a result of experience with the Mark IA, the Mark II programme will initially stress the development of high-reliability cells by the industrial contractors, Eagle–Picher Industries Inc.† and Gould Inc.†

The performance goals of the Mark II cells are 125 W h kg^{-1} at the 4-hour discharge rate, 125 W kg^{-1} at 50% discharge, and a maximum of 20% energy lost after 800 deep discharge cycles. An additional requirement of this programme is to use cell fabrication techniques and components that are potentially low cost. The development of cells to meet these performance goals is a difficult task. The analysis described in this paper will be used to reduce the number of multiplate cell tests required to evaluate the numerous variables that effect cell performance. This technique should increase our chances of optimizing the Li–Al/iron

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† Cost given in 1979 dollars.

† Eagle–Picher Industries Inc. and Gould Inc. are two of the ANL subcontractors for cell and battery development.

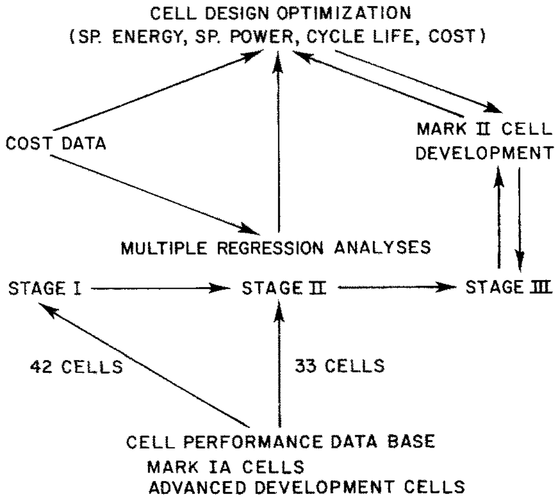

Fig. 1. Multiple regression analysis strategy.

sulphide cell design with respect to specific energy, specific power and cycle life.

2. Multiple regression analysis

Elements of the multiple regression analysis strategy are shown in Fig. 1. The original data base for this analysis (Stage I) consisted of performance data from 42 Li–Al/FeS and Li–Al/FeS_2 cells having many different designs and operating modes; these cells were fabricated either by ANL, Eagle–Picher or Gould. The performance data from tests of these cells have been summarized in earlier reports [7, 8].

Cell design variables included in Stage I were electrode thickness, active material composition, volume fraction of electrolyte in the electrodes, properties of the electrode separator, charge state at cell fabrication, cell compactness, cell resistance and number of electrode plates. Operating variables included discharge rate, coulombic efficiency, charge and discharge cut-off voltages, discharge current density and electrode utilization.

A multiple regression analysis was conducted to develop equations of the general form

$$\hat{y} = b_0 + b_1X_1 + b_2X_2 + b_3X_3.$$

In this equation b_0, b_1, b_2 and b_3 are constants, X_1, X_2 and X_3 are independent variables and $\hat{y}$ is the dependent variable (specific energy or specific power). The specific-energy equation determined in Stage I only applied to the first 20 cycles of cells operated between 400 and 430° C. Since the specific energy of the lithium/iron sulphide cell is highly dependent upon cell temperature and cycle number, performance data from 33 cells were subsequently used (Stage II) to obtain an equation for specific energy at a given cycle number, with cell temperature as an independent variable.

Trial and error techniques were used to develop equations of the type shown above such that the difference between the experimental and calculated dependent variables met certain statistical criteria [9]. The number of independent variables used in the equation was based on the minimum number required to significantly lower the standard deviation of the error. Tests used for the error included the runs, normal distribution and scatter tests [9]. The runs and scatter tests indicate whether the errors are random and independent. Run values of ± 1 are favourable and values around ± 2 are marginal. The normal-distribution test includes a test for skewness and kurtosis (related to deviations from the normal bell-shaped curve for the normal distribution). Kurtosis values of ± 1 and skewness of ± 0.5 are favourable. The correlation coefficient, designated in this paper as R^2, was also used to evaluate the accuracy of the regression analysis [10]. A value of R^2 of 1 indicates perfect correlation between the calculated and measured values.

2.1. *Specific power*

The specific-power equation resulting from the multiple regression analysis was as follows:

$$\ln(\mathrm{SP}) = 0.28 + 0.86\ln(\mathrm{PF}) + 0.12\ln(\mathrm{CF}) + 0.32\,\mathrm{FCCF} \qquad (1)$$

where $\mathrm{PF} = (\mathrm{OCV})^2/(4\bar{R}_c W)$. As illustrated in Fig. 2, the measured specific power and that calculated from Equation 1 for the 26 cells used in the regression analysis showed good agreement. The statistical tests were all favourable: runs = 1.26, skewness = 0.27, kurtosis = 0.91, R^2 = 0.95, and acceptable scatter test. As a further check of Equation 1, the specific power was determined for 16 cells not used in the regression analysis and these values then compared to calculated values from Equation 1. As can be seen in Fig. 3, there is

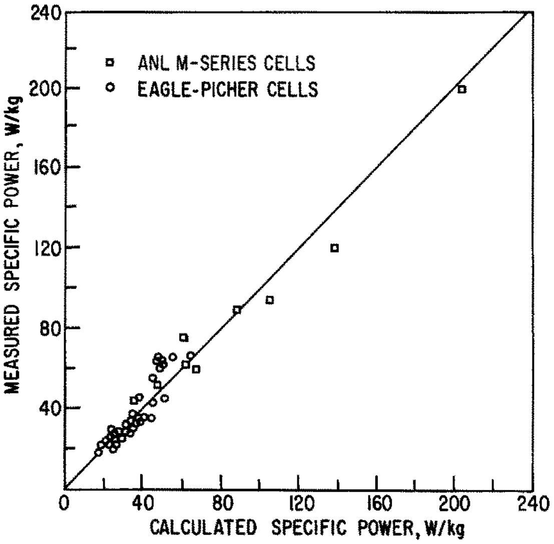

Fig. 2. Calculated and measured specific power of Li–Al/FeS and Li–Al/FeS$_2$ cells.

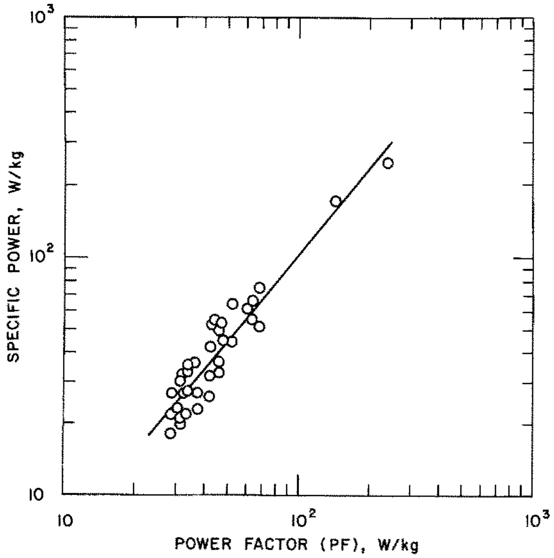

Fig. 4. Contribution of the power factor to the specific power of Li–Al/iron sulphide cells.

good agreement between the predicted and measured specific powers for these cells.

Selection of suitable dependent and independent variables in Equation 1 requires knowledge of the electrochemistry of the system as well as the requirement of meeting certain statistical tests. For example, a plot of specific power versus the power factor, PF, showed that the open-circuit voltage and peak current were major contributing factors to the peak specific power, as would be expected. This result is shown in Fig. 4. The logarithmic function resulted because of the scatter in the experimental data, i.e., the logarithm reduces the spread or range of values for the variable and makes identification of a suitable fit to the data much easier. Another example of the requirement for knowledge of the system can be shown for the remaining terms in Equation 1. It has been observed experimentally that the open-circuit voltage of Li–Al/FeS cells increases after a larger number of cycles. This behaviour is believed to be related to the increase in lithium composition at the front of the Li–Al electrode with repeated cycling. Examination of Li–Al electrodes operated over a large number of cycles has shown a higher lithium composition at the electrode interface nearest the positive electrode. This behaviour is believed to result in the need for the last two terms in Equation 1, which are identified as a charge factor, CF, and a fully charged correction factor, FCCF. The dependence of the specific power on these variables is shown in Fig. 5. The contribution of these terms to the specific power is significant, but much less than that for the power factor.

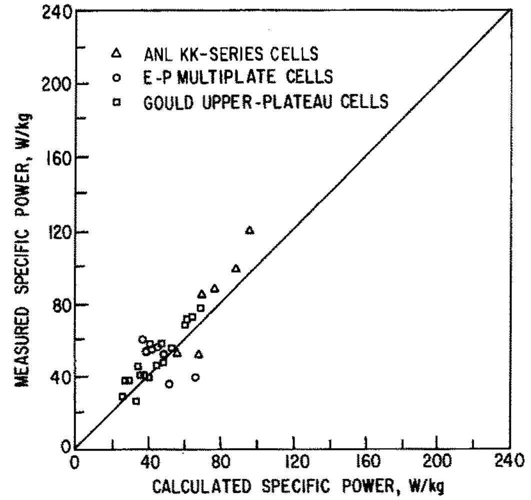

Fig. 3. Post-sample check of measured and calculated specific power.

2.2. *Specific energy*

The initial specific-energy equation developed in this study was limited in its application because of the temperature and cycle-life restrictions [1]. A

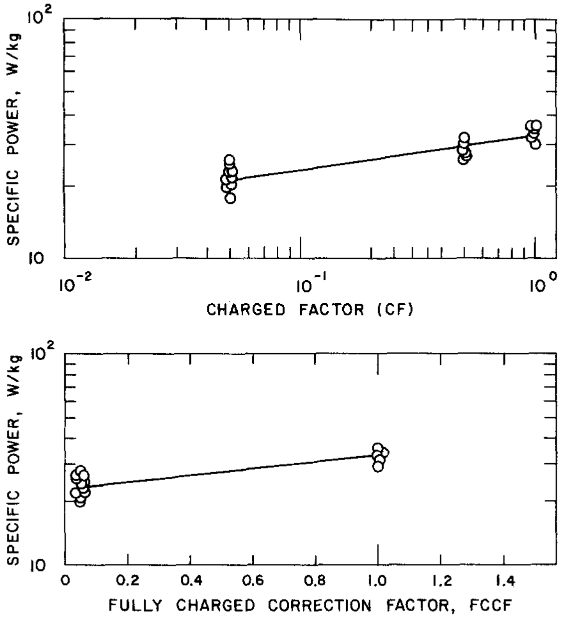

Fig. 5. Contribution of the charge factors to the specific power of Li–Al/iron sulphide cells.

later analysis, Stage II of the regression strategy, included these variables in the specific energy equation. The range of variables used to develop this specific energy equation is shown in Table 1. From multiple regression analysis of performance data for 33 cells, the following equation for the specific energy of a cell at a given cycle number was obtained:

$$\begin{aligned}\text{SPECYC} = {} & 25.210 + 0.442\ \text{SPEBAS} + 0.411\ \text{FSLMUL} \\ & + 0.271\ \text{FSUBL} + 47.442\ \text{VFSNEG} \\ & - 59.373\ \text{VFSPOS} - 0.009\ \text{PPXCYC}.\end{aligned} \tag{2}$$

In Equation 2, FSLMUL is defined by

$$\begin{aligned}\text{FSLMUL} = {} & 51.146 + 0.316\ \text{VOLT2R} + 0.665\ \text{VOLT1R} \\ & + 0.137\ \text{AHREFF} + 24.287\ \text{VFSPOS} \\ & + 56.418\ \text{TEMPR} - 17.590\ \text{POSPIN} \\ & - 0.359\ \text{OFFEUT} - 91.757\ \text{VFSNEG} \\ & - 14.057\ \text{NSPTHC}\end{aligned} \tag{3}$$

where

$\text{VOLT1R} = (\text{OCV} - \text{DCO})/A_e i_D \bar{R}_c$

$\text{VOLT2R} = (\text{CCO} - A_e i_D \bar{R}_c - \text{DCO})/A_e i_c \bar{R}_c$

TEMPR = (cell operating temperature − 450° C)/450° C

OFFEUT = LiCl composition of the electrolyte − 44.2 wt%

FSUBL = FSLMUL/MUL

MUL = 0.01 (theoretical cell capacity) (OCV − DCO)/W.

Table 1. Variables used in the multiple regression analysis of cell specific energy and specific power

Variable	*Range*
Fraction of charge (as fabricated)	0.05–1.0
Electrode area	270–1806.5 cm^2
Separator thickness	0.2–0.64 cm
Limiting electrode thickness[†]	0.2–0.63 cm
Counter electrode thickness	0.25–1.0 cm
Limiting electrode capacity density	0.64–1.6 A h cm^{-3}
Volume fraction salt in positive electrode (charged state)	0.4–0.8
Volume fraction salt in negative electrode (charged state)	0.2–0.6
Negative-to-positive theoretical capacity ratio	0.6–1.5
Cu_2S composition[‡]	0–25 wt%
LiCl composition of electrolyte	44–54 wt%
Average cell resistance	1.2–13.3 mΩ
Discharge current density	0.01–0.18 A cm^{-2}
Charge current density	0.03–0.04 A cm^{-2}
Temperature	410–525° C
Number of cycles	28–1300

[†] Half-electrode thickness.

[‡] An additive used in the positive electrode to improve performance.

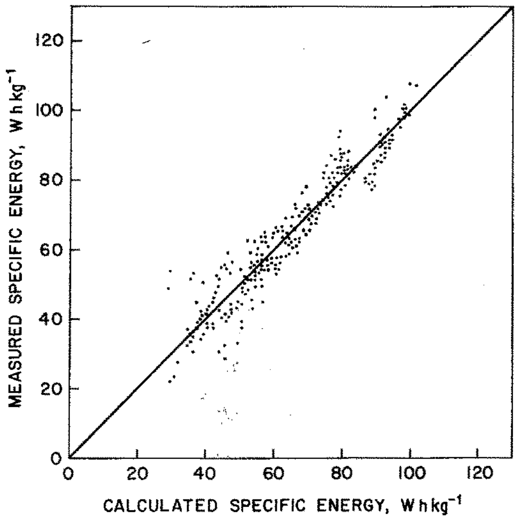

Fig. 6. Calculated and measured specific energy at a given cycle for 19 Li–Al/iron sulphide cells (Cell nos.: M-4, M-8, 1A6, M-MP-3, I3B1, I3C2, 1B4, 1B6, 2A5, 2B8, I-8-H-040, G-04-033, and EPMP-7-17, -33, -46, -55, -56, -62 and -63).

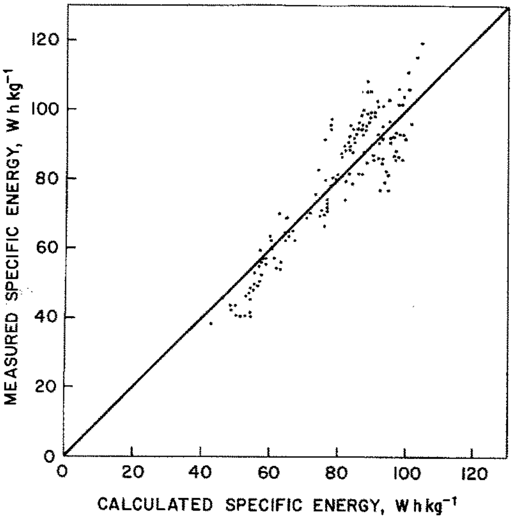

Fig. 7. Post-sample check of calculated and measured specific energy at a given cycle for 14 Li–Al/iron sulphide cells (Cell nos.: M-2, M-6, M-7, KK-5, I3B2, I3C1, 2B6, I-8-F17, EPMP-7-31, -32, -57, -71, -75 and -86).

The variable SPEBAS is the specific energy of the cells during the initial cycles (< 25 cycles) and is defined by

$$\begin{aligned}\mathrm{SPEBAS} = {} & 141.350 + 0.631\ \mathrm{FSLMUL} - 2.722\ \mathrm{TSUBCR} \\ & - 48.032\ \mathrm{VFSPOS} - 0.052\ \mathrm{FSUBL} \\ & - 37.453\ \mathrm{NSPTHC} - 29.754\ \mathrm{TEMPR} \\ & - 11.744\ \mathrm{POSPIN}\end{aligned} \tag{4}$$

where TSUBCR = counter electrode half-thickness/separator–retainer thickness.

As can be seen in Figs. 6 and 7, the calculated and measured specific energies at a given cycle for the cells used in the multiple regression analysis are in good agreement (± 10% error). The cells for which the data are shown in Figs. 6 and 7 included the following: six Li–Al/FeS bicells fabricated by Eagle–Picher (1A6, I-3B-2, I-3C-1, I-3B-1, I-3C-2, 1B4) and three by ANL (M-6, M-8, KK-15); five Li–Al/FeS_2 bicells fabricated by Eagle–Picher (2A5, 2B6, 2B8, I-8-040, I-8F-17), three by ANL (M-2, M-4, M-7) and one by Gould (G-04-003); and fourteen Li–Al/FeS multiplate cells fabricated by Eagle–Picher (EPMP-5-017, EPMP-7-031, -032, -033, -036, -046, -055, -056, -057, -062, -063, -071, -075, -086) and one by ANL (M-MP-3). Data from the cells in Fig. 6 were used to develop the specific energy equations and data from the cells in Fig. 7 were used as a check of the predictive capability of the equations. The correlation coefficient (R^2) was determined for the experimentally determined values and those calculated from Equations 2–4. The values of R^2 were found to be 0.90 for Equation 2, 0.79 for Equation 3 and 0.75 for Equation 4; these results indicate good correlation. In addition, the standard deviation of the residuals (the difference between the calculated and measured values) was found to be 5.75 for Equation 2, 4.79 for Equation 3 and 8.77 for Equation 4; these results also indicate good correlation.

Clues to the independent variables to be used in Equation 2 were obtained from the general shape of the specific energy versus cycles curve described in the next section of this paper. The Li–Al/iron sulphide cells show a peak specific energy early in the cycle life and a subsequent decline in specific energy with further cycling. As stated earlier, the SPEBAS term represented the peak specific energy of cells during the early cycles. The FSLMUL term is a major contributing factor to the specific energy and represents the dependence of the specific energy on the average cell discharge voltage, utilization, theoretical capacity and cell weight in terms of cell design and operating variables. The other terms in Equation 2 are significant, but minor terms compared to the first three independent variables.

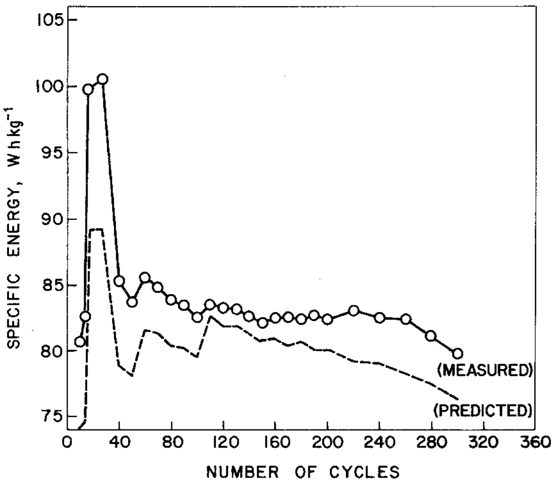

Fig. 8. Measured and predicted specific energy as a function of cycles for Cell EPMP-7-055.

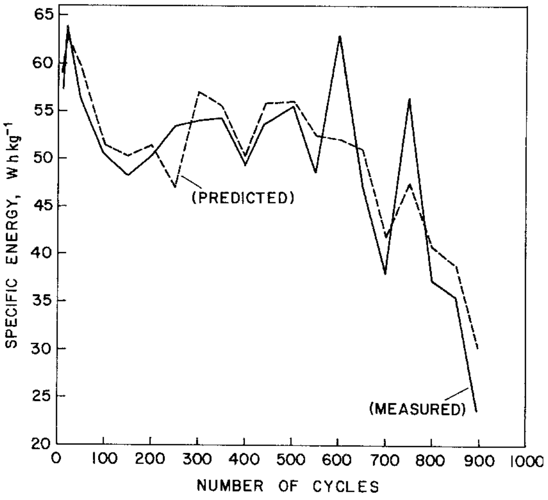

Fig. 10. Measured and predicted specific energy as a function of cycles for Cell I-3B-1.

Plots similar to those shown in Figs. 4 and 5 were used to identify suitable independent variables for the multiple regression analysis.

3. Cell cycle-life characteristics

The measured and calculated specific energies as a function of cycle number are shown for Cell EPMP-7-055 in Fig. 8, for Cell M-8 in Fig. 9 and for Cell I-3B-I in Fig. 10. These figures show that the predictive capability of Equation 2 is very good. The many sharp fluctuations in the specific energy shown in these figures were due to changes in the operating conditions of the cell, i.e., changes in temperature, charge or discharge cut-off voltages and charge or discharge current densities. Even under these conditions, the calculated specific energy is in good agreement with the measured value.

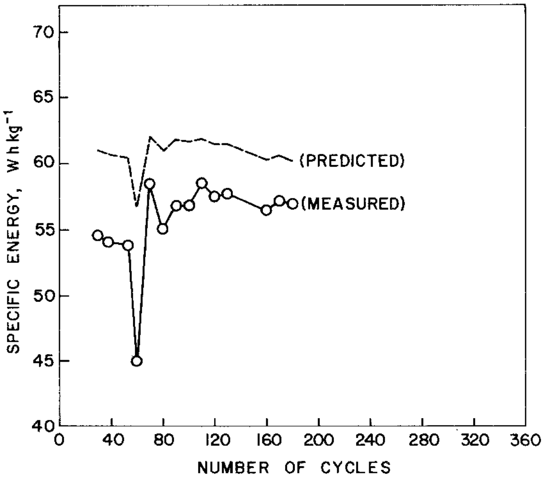

Fig. 9. Measured and predicted specific energy as a function of cycles for Cell M-8.

The general shape of the specific energy versus cycles curve for the Li–Al/FeS cells, under constant operating conditions, is as follows: first there is an increase in the specific energy from that at start-up to a peak specific energy within about 20 cycles, then a region in which the specific energy decreases rapidly from the peak value, and finally a region of nearly constant decline in specific energy with cycling at a rate of between 0.02 and 0.04%/cycle.

The percentage specific energy decline per cycle versus the number of cycles is shown for six Li–Al/FeS bicells (LiCl-rich electrolyte) in Fig. 11 and for six Li–Al/FeS multiplate cells (eutectic electrolyte) in Fig. 12. The curves drawn in these figures were calculated from Equation 2 and show good agreement with the performance data. Overall, the bicells showed a much lower decline in specific energy with cycling than the multiplate cells. For example, the cycle life projected to occur before a 20% decline in specific energy was found to be 800 cycles for the bicells and only 400 cycles for the multiplate cells at 460° C. Fig. 12 also shows the effect of temperature on the specific energy decline rate with cycling, as predicted by Equation 2. A 40° C temperature

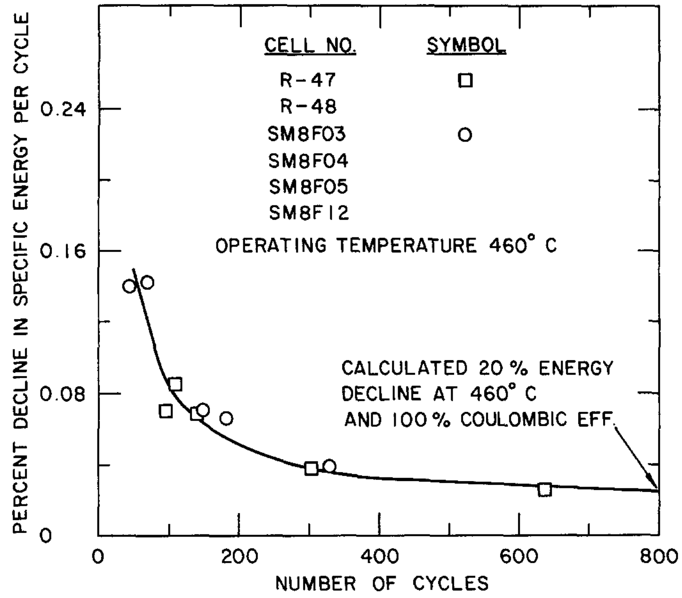

Fig. 11. Specific energy decline of Li–Al/FeS bicells (LiCl-rich electrolyte).

increase, from 440° C to 480° C, increases the cycle life for the multiplate cell from 300 cycles to 500 cycles.

4. Cell design study

A cell design study was conducted [11] covering the large number of variables affecting cell performance. Equations 1 and 2 were used to predict the performance for up to 800 cycles of 84 Li–Al/FeS multiplate cell designs. The following design variables were investigated: positive-electrode thickness (0.28 to 0.52 cm), volume fraction of salt in the positive electrode (0.38 to 0.67), positive-electrode loading density (0.7 to 1.6 A h cm^{-3}), negative electrode thickness (0.28 to 1.14 cm) and negative-to-positive capacity ratio (1.0 to 1.3); all other design variables were held constant. The results indicated that the optimal performance under these conditions will be achieved by a cell with thin electrodes (e.g., 0.28 to 0.36 cm thickness for the positive electrode), a negative-to-positive capacity ratio greater than one and an initial capacity loading density of 1.4 to 1.6 A h cm^{-3}. This combination of variables results in the lowest rates of specific energy decline with cycling and highest specific energy. The results of this study indicated the most likely cell designs to meet the electric-vehicle battery performance goals. These designs were included in an experimental programme with engineering-scale Li–Al/FeS cells for further performance evaluation.

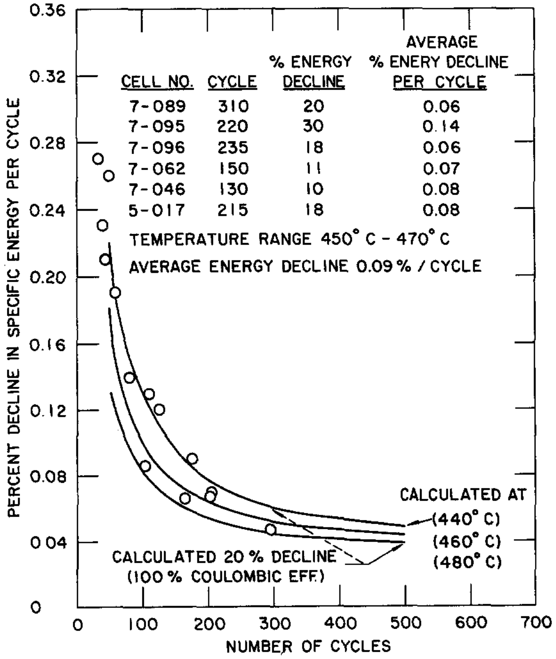

Fig. 12. Specific energy decline of multiplate cells (eutectic salt).

Equations 1 and 2 were valuable in that prediction of the performance of the 84 design cells was possible based on a limited amount of test data for a given cell size and cell type (bicell or multiplate). Without these equations, one would normally use extrapolations of performance data and assumptions on the performance of the design chosen, and this method would have been much less reliable.

5. Conclusions

(a) Over the range of variables used in the multiple regression analysis, empirical equations have been developed to predict specific energy (as a function of the number of deep discharge cycles) and specific power, and these equations can be used to obtain a quantitative estimate of the effects of a number of design and operating variables on cell performance.

(b) This technique of data analysis has proved useful in identifying the most likely cell designs to meet electric-vehicle battery performance goals and, therefore, reduces the cell testing and effort required to find the optimum cell design.

(c) The specific energy equation can be used to calculate the percentage specific energy decline per cycle.

(d) As new performance data are generated in the cell test programme, these results can be added to the regression analysis in order to expand the range of variables over which the performance equations are valid.

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