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OPTIMIZATION OF THE LITHIUM/THIONYL CHLORIDE BATTERY

A FINAL REPORT

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ABSTRACT

This final report includes the progress which has been made in modeling the lithium/thionyl chloride cell over the past year and proposed research work for the coming year. A one-dimensional mathematical model for a lithium/thionyl chloride cell has been developed and used to investigate methods of improving cell performance. A paper on this work has been submitted to the *Journal of the Electrochemical Society* for publication. During the course of this work a problem was detected with the banded solver being used. Another banded solver was investigated and found to be more reliable. A technical note on this work with banded solvers has been submitted to the *Journal of the Electrochemical Society* for publication. Future work may take one of two directions depending upon discussions with Bob Bragg. The one-dimensional model could be augmented to include additional features and to investigate in more detail the cell temperature behavior, or a simplified two-dimensional model for the spirally wound design of this battery could be developed to investigate the heat flow within the cell.

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INTRODUCTION

The objective of the work over the past year was to to develop a model of the lithium/thionyl chloride ($Li/SOCl_2$) cell which can be used to

1. aid in understanding the physical phenomena occurring in the cell,
2. reduce time intensive and costly experimental work, and
3. expedite the finding of acceptable and safe, yet optimal, designs.

This objective has been partially satisfied by the one-dimensional mathematical model which has been developed. Possible future work includes augmenting this one-dimensional model and developing a two-dimensional model in order to further investigate the $Li/SOCl_2$ cell and pursue in more depth the three items listed above.

WORK COMPLETED

A one-dimensional mathematical model for a lithium/thionyl chloride cell has been developed and has been used to investigate methods of improving cell performance. A paper describing this work has been submitted to the *Journal of the Electrochemical Society* for publication and is listed in appendix A. The independent design criteria are identified and it is shown which of these criteria are most influential in affecting cell performance. The model is used to show how improved cell lifetime and voltage can be achieved by changing certain of these criteria. A better understanding of the physical phenomena occurring in the $Li/SOCl_2$ cell has been gained by studying the model predictions. For example, the effect of the LiCl film on cell performance is now better understood; dense films, formed during high temperature storage, will cause low operating voltages, early cell failure, and elevated cell temperatures which could, perhaps, lead to thermal runaway. Please refer to appendix A for the literature review, model development, and results of this work.

During the course of this work a problem was detected with the banded solver being used, Newman's BAND algorithm (1, 2). Another banded solver, deBoor's method (3), was investigated and found to be more reliable. A technical note on this work with banded solvers has been submitted to the *Journal of the Electrochemical Society* for publication and is listed in appendix B.

PROPOSED FUTURE RESEARCH WORK

Future work would include the improvement of the present one-dimensional model and the development of a two-dimensional model. The one-dimensional model could be augmented to include additional features of the physical system and the two-dimensional model would be useful for investigating the heat transfer within the cell itself.

Further Development of the One-Dimensional Model

The present model could be augmented to include additional features in order to investigate their effects on cell performance. These improvements would include the addition of the Cl^-, SO_2, and S species, the growth of the LiCl film as the cell discharges, modeling a stack of cells representing the cross section of an entire $Li/SOCl_2$ battery, and accounting for porous electrode swelling during the discharge. Also, the cell energy balance could be modified to include more complex heat transfer paths. For example, the heat transfer from the cell to the battery pack in which it is contained and from the battery pack to the surroundings could be included in the model.

The model could also be used to estimate the kinetic parameters of the electrochemical reactions occurring at the electrodes within the cell. This is important information which would be used by experimenters and designers to improve cell materials. A parameter estimation technique, along with experimental data and complete cell specifications, would be used in conjunction with the model in order to accomplish this goal.

Two-Dimensional Thermal Model

A two-dimensional thermal model similar to the one-dimensional thermal model presented by Szpak *et al.* (4) could be developed for the jellyroll configuration of

the $Li/SOCl_2$ battery (Fig. 1). The model equations would consist of a differential energy balance and a simplified differential material balance equation. These equations would be solved in each region of the cell (shown in Fig. 2) in both the r and θ directions.

Assuming that the heat transfer in each region of the cell is due almost exclusively to conduction, the differential energy balance for a given region would be written as

$$\left(\rho_e c_{p,e}\epsilon + \rho_m c_{p,m}(1-\epsilon)\right)\frac{\partial T}{\partial t} = \lambda\nabla^2 T + \sum_j q_j \qquad (j = 1, 2, ...) \qquad [1]$$

where $c_{p,e}$ and $c_{p,m}$ are the heat capacities of the electrolyte and matrix phases of the region, respectively. The q_j terms in Eq. [1] represent various heat sources and sinks. Two such sources would be included as was done in the model by Szpak *et al.* (4). These sources would be q_1 and q_2 where q_1 would represent all energy changes arising from joule heating such as internal short circuits and q_2 would represent all energy changes arising from intrinsic sources such as the heat produced by thermally activated exothermic reactions.

A simplified material balance would be used to calculate the electrolyte concentration, c, which would be needed to calculate q_2 in Eq. [1]. The material balance would be simplified by assuming that the flux of electrolyte is due to diffusion only. The material balance would be

$$\frac{\partial(\epsilon c)}{\partial t} = D_{eff}\nabla^2 c + R_i \qquad [2]$$

R_i in Eq. [2] is a sink term accounting for the changes in concentration due to thermally activated reactions. That is, R_i would be set to zero until some critical temperature is reached, such as the melting point of lithium. Szpak *et al.* (4) choose to use a first order reaction rate expression for R_i which may be considered in future work on this project.

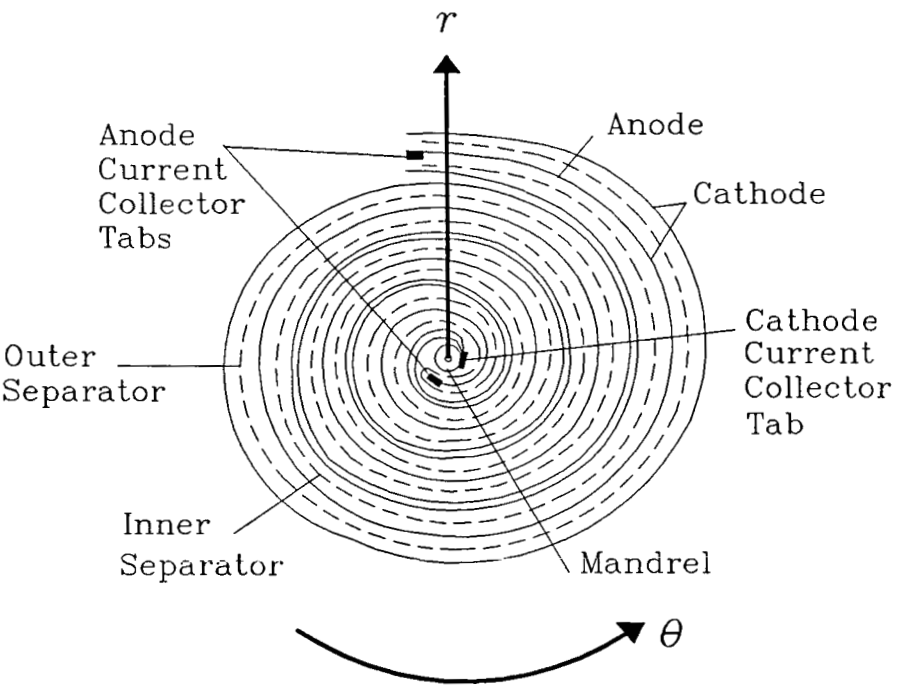

Figure 1. Schematic representation of the spirally wound (jellyroll) configuration of the $Li/SOCl_2$ battery

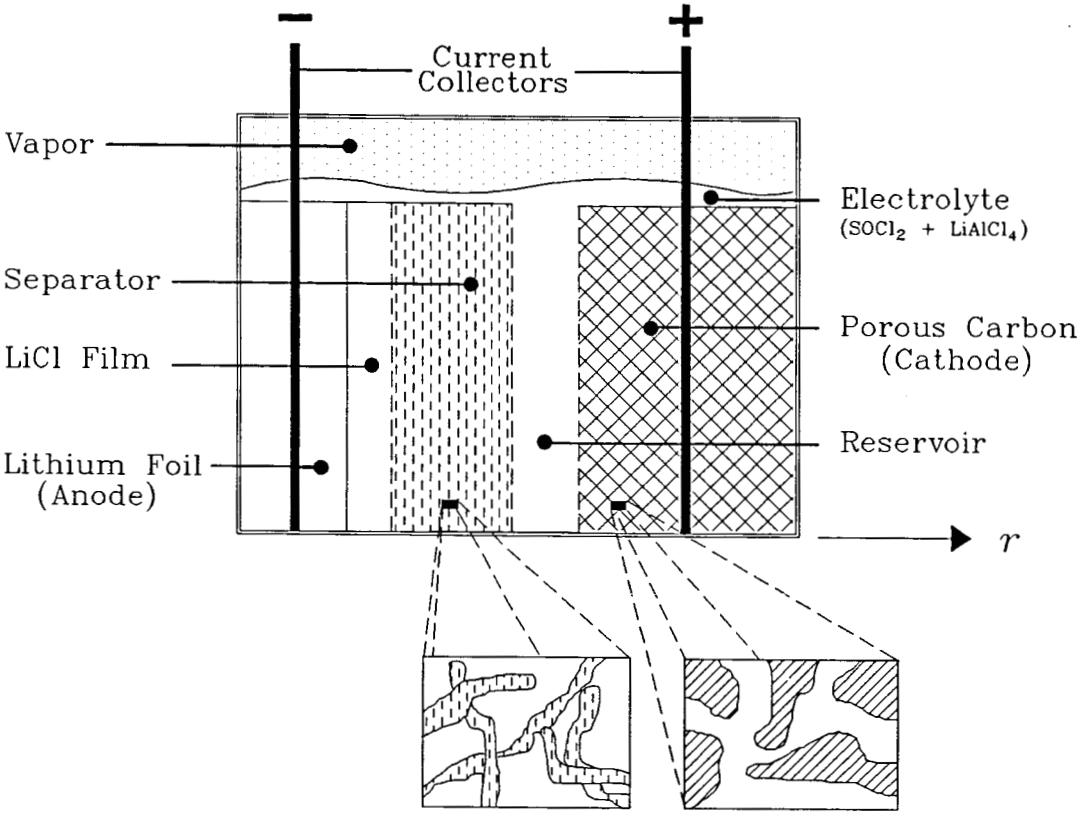

Figure 2. Schematic representation of an individual $Li/SOCl_2$ primary cell

To date, Eq. [1] and [2] have been written for two-dimensions, r and θ, and dedimensionalized. The two resulting dimensionless equations could be solved numerically, using a finite difference algorithm (3, 5), to determine the two-dimensional temperature and concentration profiles of the jellyroll configuration of the $Li/SOCl_2$ cell. This model would be used to determine if better heat transfer paths could be created (e.g., by using thicker or extra Li foils) so that a safe high-rate $Li/SOCl_2$ battery could be designed. Also, the concentration profiles in the r dimension would be compared to those obtained using the more sophisticated one-dimensional model described above to determine if significant deviations exist and whether or not Eq. [2] would need to be modified.

LIST OF SYMBOLS

c	concentration of the electrolyte, mol/cm^3
$c_{p,i}$	specific heat of material i, J/gK
D_{eff}	effective diffusion coefficient of electrolyte, cm^2/s
q_j	jth heat source or heat sink, W/cm^3
r	radial dimension, cm
R_i	production rate of species i due to reaction, mol/cm^3s
t	time, s
T	cell temperature, K

Greek Symbols

ϵ	void volume fraction
θ	angular dimension, cm
λ	thermal conductance, W/cm^1K
ρ_i	density of material i, g/cm^3

Subscripts

e	electrolyte
i	species i
m	matrix material

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