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An Integrated Model of the Lithium/Thionyl Chloride Battery

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Abstract

The desire to reduce the time and cost of design engineering on new components or to validate existing designs in new applications is stimulating the development of modeling and simulation tools. We are applying a model-based design approach to low- and moderate-rate versions of the $Li/SOCl_2$ D-size cell with success. Three types of models are being constructed and integrated to achieve maximum capability and flexibility in the final simulation tool. A phenomenology-based electrochemical model links performance and the cell design, chemical processes, and material properties. An artificial neural network model improves computational efficiency and fills gaps in the simulation capability when fundamental cell parameters are too difficult to measure or the forms of the physical relationships are not understood. Finally, a PSpice-based model provides a simple way to test the cell under realistic electrical circuit conditions. Integration of these three parts allows a complete link to be made between fundamental battery design characteristics and the performance of the rest of the electrical subsystem.

Introduction

An ongoing revolution is occurring in the processes by which complex components and systems are developed and designed. Timetables for delivering new products continue to shrink along with the resources that can be made available to complete the necessary engineering tasks. The time-consuming build and test approach for determining whether a particular design can meet a new set of requirements is not compatible with this new environment. Increasing reliance is being placed on modeling and simulation tools to achieve the improvement in efficiency of the design process that will be needed in the future. In addition to enabling faster and cheaper design development, modeling can also optimize manufacturing processes, focus research on improved materials, and promote better understanding of component reliability and life as well.

We are applying this philosophy to the design of power sources, beginning with the lithium/thionyl chloride battery system. While appearing simple on the surface, batteries are complex chemical systems that in many cases are only partially understood on a fundamental level, especially once the full range of operating environments and conditions is considered. In the past, many attempts have been made to model electrochemical systems with varying degrees of success. The inability to construct explicit mathematical and chemical descriptions for all of the cell processes, or for that matter to measure all of the physical parameters needed to populate such a model, ultimately becomes a limiting factor. One way to address this limitation is by including empirical parameters, although even in this case the need for certain parameters may not be recognized. However, using incomplete cell process descriptions makes it much more difficult to reliably relate changes in battery performance to details of the design or to the material properties and reduces flexibility to easily handle a variety of cell designs.

Since the prospect of completely describing all of the physical relationships in a battery system, especially one as complicated as lithium/thionyl chloride, seemed rather unlikely, several modeling approaches have been investigated in parallel. A phenomenological model has been constructed that uses as much of the available information on cell processes as possible, and an artificial neural network (ANN) model has been assembled in order to improve computational efficiency and eliminate the necessity to measure all of the physical constants for the cell. In addition, a PSpice battery model has been included to make it simpler to express the simulation results and to allow an easier interface with the balance of a complete electrical circuit. Integrating these three portions of the battery model will enable the full power of the modeling approach to be realized by taking advantage of the strengths of each of the individual parts.

DISCLAIMER

Lithium/Thionyl Chloride Cell

The lithium/thionyl chloride D-size cell simulated in this work is a design that has been developed and extensively characterized by Sandia National Laboratories over several years.[1-3] Three variations of the cell are being studied, a low-rate cell for discharge rates up to 70 mA, a moderate-rate cell for discharge rates up to 500 mA, and a high-rate cell for discharges up to 5 A. Models will eventually be implemented for all three cells, although only the low- and moderate-rate designs have been simulated thus far. Table 1 shows some of the salient parameters for the three design variations. All are spiral wound, use the same D-size can, contain a $LiAlCl_4$ electrolyte salt, and are cathode limited for safety and long life.

Table 1: $Li/SOCl_2$ Cell Design Parameters

	Design		
	Low	Moderate	High
Anode Area (cm^2)	145	344	508
Cathode Area (cm^2)	179	394	540
Cathode Thickness (cm)	0.183	0.076	0.064
$LiAlCl_4$ Concentration (M)	1.0	1.0	1.5
Theoretical Li Capacity (Ah)	17.6	16.2	13.3
Theoretical Electrolyte Capacity (Ah)	19.3	19.3	17.0

An extensive series of capacity tests has been completed for both the low- and moderate-rate cell designs, and provides the basis for either validating and adjusting the parameters in the phenomenological model, or training and validating the ANN model. Cell capacities were measured over a range of temperatures and for a variety of constant-resistance loads. Figure 1 shows the capacity results for the low-rate cell in the form of a surface plot. Maximum capacity of about 15.5 Ah is delivered near ambient temperature and when the load resistance is larger than 250 ohms (~15 mA current). The capacity versus temperature curves at a given load are sigmoid in shape.

Electrochemical (Phenomenological) Model

The electrochemical model is based on mass and energy balance within the cell, the internal mass transport, a

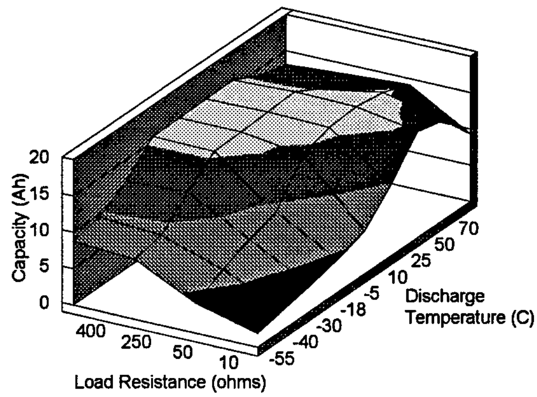

Figure 1: *Capacity versus temperature and load resistance for low-rate $Li/SOCl_2$ D-size cells.*

standard Butler-Volmer description of the electrode kinetics, and a bulk description of the cathode porosity and plugging profile versus depth. Other factors, such as self-discharge, are represented by separate subroutines built to duplicate experimental data measured on the same type of cells. One parameter that has not been included yet is the time- and temperature-dependent formation of the lithium chloride corrosion film on the surface of the lithium anode. Some experimental measurements of the film resistance are available from ac impedance data, but the variation with different conditions is very complex. An ANN model of the changes in film resistance may be necessary to simulate the complicated nature of this space, but at present there are not yet enough impedance test data to train a network, although this is an area of current effort.

Kinetic and transport parameters were obtained by matching simulated cell capacities and average cell voltages to constant load discharge curves over a range of temperatures and loads. Cathode swelling was accounted for by adjusting the cathode porosity and thickness to match cell capacity at ambient temperature and high load resistance (i.e., low current). The resulting model fits constant-load, constant-external-temperature discharge curves quite well, as shown in Figure 2.

Artificial Neural Network (ANN) Model

ANNs are inductive, or data-based, models for simulating input/output mappings. Although this study represents their first application to chemical power

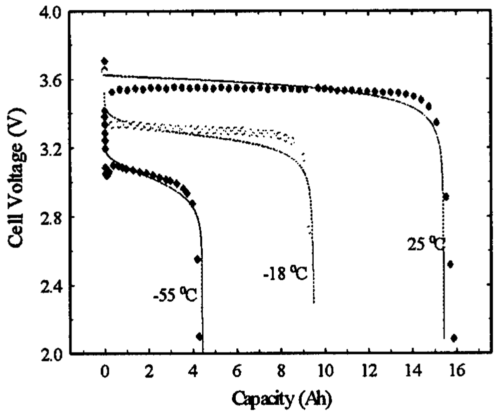

Figure 2: *Simulated (line) vs. experimental (symbol) discharge curves for low-rate Li/SOCl$_2$ cells discharged into 50 ohms.*

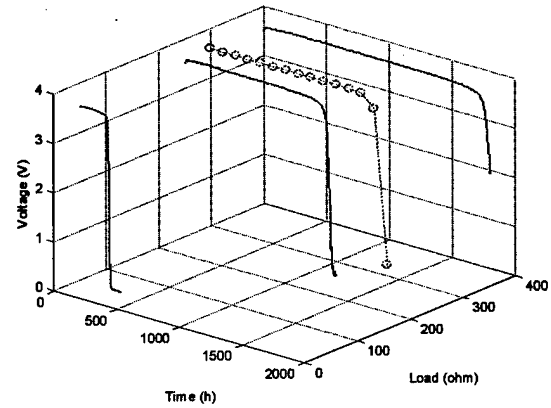

Figure 3: *Interpolated discharge curve at 300 ohms predicted for the low-rate Li/SOCl$_2$ cell by the BPN.*

sources, they have been used to simulate many other types of complex systems. Their computational efficiency is an advantage, particularly when multiple response or prediction computations are required. In the present case, the inputs included the battery temperature, the load resistance, and the initial state-of-charge. The outputs were voltage, current, and deliverable capacity. Examples of correct system behavior for training the ANNs were obtained from the same set of capacity data used to optimize and validate the electrochemical model. Interpolation within this space is allowed using the ANNs, but extrapolation is not recommended.

Several ANN architectures were investigated to identify those most appropriate for use with power sources. The first was an extension of the radial basis function network called the connectionist normalized linear spline (CNLS) network.[4] The CNLS net is very good at local approximations and simulated the knee in the discharge curves very well. However, the CNLS network does not have the interpolation capability that is needed for the simulation of power source behavior, so other ANNs were also evaluated.

The most useful ANN structure for power source applications was the layered perceptron network trained by feedforward back propagation (BPN),[5,6] which also happens to be the most widely used ANN. As shown in Figure 3, the BPN also is capable of simulating Li/SOCl$_2$ cell discharge curves quite accurately, and provides the needed interpolation capability.

In order to handle temperature variation and pulse loads, the strategy employed was to use the BPN trained on the constant-load and temperature data, moving between the appropriate interpolated load curves whenever temperature or load changes during the discharge. This approach worked very well and is illustrated with a simple example in Figure 4. In this example, 3 Ah of capacity were removed alternately at each load. The rapid drop in cell voltage at the end of the discharge is predicted well. More complicated patterns of temperature and load are easily programmed and tested.

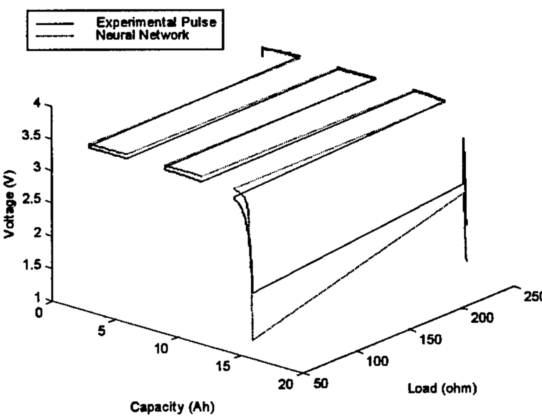

Figure 4: *Comparison between experiment (—) and simulation (···) for a low-rate Li/SOCl$_2$ cell undergoing an isothermal pulse load between 50 and 250 ohms.*

PSpice Model

A battery discharge simulator has been published for the electrical circuit simulation program PSpice.[7,8] This model has been extended to the Li/SOCl$_2$ battery system, and has been found to reproduce battery discharge voltage and capacity quite well as shown in

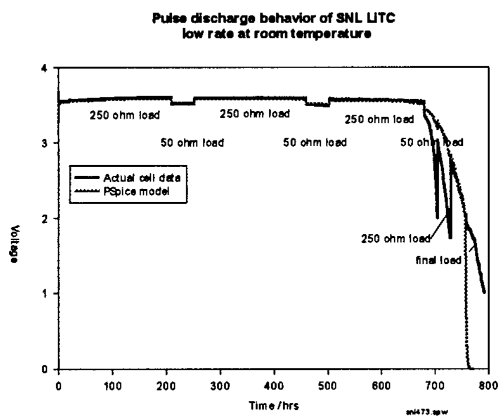

Figure 5: *PSpice simulation of a low-rate Li/$SOCl_2$ cell discharge curve where the load alternates between 250 and 50 ohms.*

Figure 5. The primary data needed to simulate this discharge curve are the battery voltage versus state-of-charge, preferably at the same discharge rate and temperature that the simulation is to be run. Other useful information that will improve the fidelity of the prediction is the total internal cell resistance as a function of the state-of-charge. These values are provided to the code in the form of lookup tables. Similar good results can be obtained for many other battery chemistries.

Integration of Model Sections

While each of these modeling approaches can provide high fidelity simulations under certain conditions, they also all have fundamental limitations that can make them difficult to use in some cases. Fortunately, the limitations are in different areas, so that combinations of the three approaches offer the potential for a very flexible modeling capability. Some of these areas have been explored. For example, the ANN model has been difficult to train correctly if 10-ohm load data are included with the 50, 250, and 400-ohm capacity results for the low-rate cell. The electrochemical model has been used to generate simulated capacity curves over the 10 to 50 ohm range, and these can be used to train the ANN, thereby saving the cost and time of making additional capacity measurements.

Another example is use of an ANN to provide values for time and temperature dependent parameters that are needed by the electrochemical model, but where the exact mathematical form of the dependence is not known. This has not been completely implemented yet, however an ANN that describes a simplified version of the anode interfacial film resistance has been interfaced to the electrochemical model and all that is needed is to collect enough impedance data to train it over the full range of possible test conditions. Others cases can be envisioned, such as providing the proper voltage and cell resistance data from both the ANN and electrochemical models to PSpice so that PSpice can be used as a virtual battery tester.

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