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High rate lithium/thionyl chloride bipolar battery development

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Abstract

The lithium/thionyl chloride (Li/$SOCl_2$) electrochemistry is capable of providing high power and high specific power, especially under pulse discharge conditions, when cells containing thin components are arranged in a bipolar configuration. This paper describes recent work concerned with bipolar cell design, cathode evaluation, component manufacturing methods, and the assembly and testing of bipolar modules containing up to 150 cells for Sonobuoy application.

Keywords: Lithium/thionyl chloride batteries; Cathodes; Bipolar cell design; Thionyl chloride

1. Introduction

The new generation of active Sonobuoys with increased detection range capability will require improvement in battery performance. The lithium/thionyl chloride bipolar design is capable of meeting the power and energy requirements of these systems (Table 1). The development of a bipolar battery design incorporating 10 in diameter thin cell components [1] was successful in fabrication and pulse testing of several full size 4-cell stacks, a 20-cell stack and a final 80-cell hermetically sealed 25 kW demonstration battery. Performance of this battery was characterized using 2, 4 and 20 ms pulses at a 10% duty cycle. A maximum pulse power of 35 kW and specific power of 1.9 kW/lb could be demonstrated at a current density of 400 mA/cm^2 [2]. Although this effort was considered a success, it did point to the need for further cell component utilization if longer pulse times are to be achieved. One goal of the present program is to develop a 10.7 kW bipolar module (one-seventh of the torpedo-size Sonobuoy power supply) with load voltage in the range from 300 to 500 V.

2. Experimental

A novel method was developed for manufacturing carbon cathodes. This method starts with a carbon slurry formulation and produces single sheets of cathode material in a sheet mold having uniform thickness and weight. Cathode thickness and carbon content are controlled by changes in the slurry formulation. This method reduced the time required for manufacturing the large numbers of cathodes required for fabrication of bipolar modules containing up to 150 cells. Full size 10 in diameter cathodes were evaluated in a special fixture with 1 in thick steel endplates separated by an O-ring which provides uniform thickness and compression during single cell tests. The final cell gap was adjusted under vacuum to provide proper compression on the cathode/separator components prior to activation with 1.6 M $LiGaCl_4/SOCl_2$ electrolyte.

Multicell stacks were fabricated from 'bipolar hardware' consisting of bipolar plates and current collecting endplates. Bipolar plates are prepared by bonding thermoplastic Tefzel material to lightly etched nickel substrates. This is an important step since the bipolar plates must maintain the correct cell gap and prevent internal electrolyte leakage between adjacent cells in a bipolar stack. The procedure is illustrated in

Table 1
Sonobuoy power supply requirements

	Torpedo size Sonobuoy	A-size [a] Sonobuoy
Power (W)	75000	4200
Volume limit (in)	10.5 (D)×36 (L)	4.5 (D)×10 (L)
Operating voltage (V)	300–500	125–250
Pulse width (s)	1–20	1–20
Duty cycle (%)	$\leqslant 10$	$\leqslant 10$
Minimum ping time (s)	400	100
Sonobuoy lifetime (days)	8	8

[a] Requirements for 10 module short-life thermal battery.

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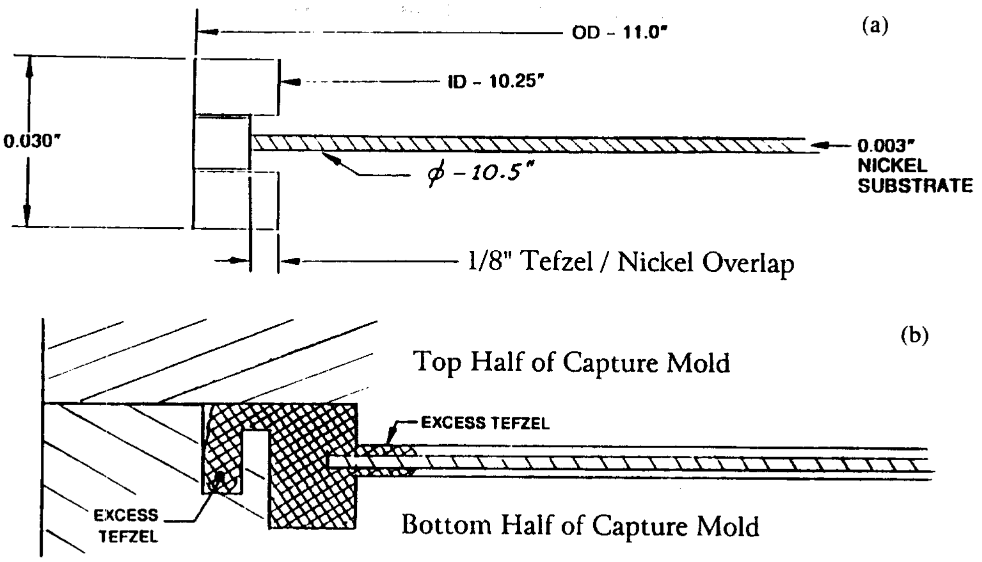

Fig. 1. (a) Tefzel/nickel sandwich prior to compression molding. (b) Tefzel/nickel substrate configuration after compression molding.

Fig. 1(a) and (b). Three Tefzel rings and a substrate are properly aligned between the top and bottom capture mold sections so as to maintain a one-eight inch Tefzel/substrate overlap, Fig. 1(a). The two sections are bolted together and maintained under compression during the heating and cooling steps. After melting, the Tefzel material forms a ring of insulation. Fig. 1(b), with the proper height sealed to the periphery of the nickel substrate. Current collecting endplates are made in a similar manner. In this case, the substrate is a nickel plated copper disk with a nickel tab terminal at the center.

A computer-controlled setup provided a constant current of 25 A during the pulse and/or continuous discharge performance tests for cathode evaluation in the special fixture. The pulses were 20 s in duration with a 10% duty cycle. After 20 cycles of pulse discharge, continuous discharge continued until the cell voltage reached 1 V. A constant power pulse discharge, 71.4 W per cell, was provided by the setup during performance tests conducted on single and multicell submodules. All cell data were stored in a Nicolet System 500 during the constant power pulse tests.

3. Results and discussion

3.1. Cathode evaluation

The variation of cathode utilization (Ah/g) with carbon loading (g/cm^2) is shown in Fig. 2. These full size cathodes were evaluated in the special fixture during continuous discharge at 25 A, i.e., 50 mA/cm^2. The novel cathodes performed better than the standard cathodes made by a calendering procedure, most likely because of the lower apparent density which increases the number of active carbon sites available for $SOCl_2$ reduction. The best result, 1.64 Ah/g, was observed for a cathode containing 4.86 g carbon, equivalent to a cathode loading of 10 mg/cm^2. All further testing was done with cells containing cathodes made by the slurry process described above.

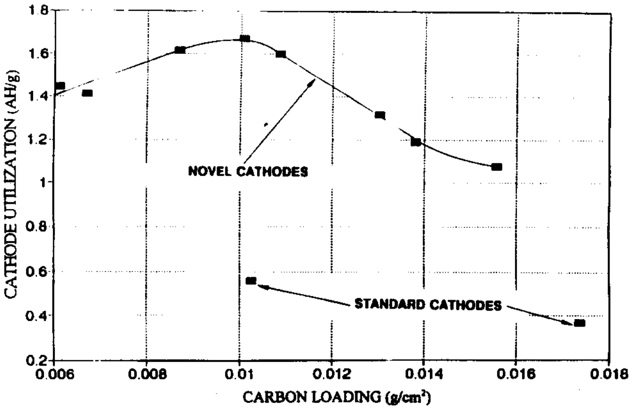

Fig. 2. Cathode utilization (Ah/g) vs. carbon loading (g/cm^2).

The initial carbon composition contained 80% of a low surface area carbon (60 m^2/g) and 20% of a high surface area carbon (> 1000 m^2/g). The effect of carbon surface area on load voltage during pulse discharge is examined in Fig. 3. The end-of-pulse-voltage (EOPV) increased to a maximum of 3 V as the high surface area component of the cathode carbon composition was increased from 0 to 60 wt.%. Additional tests confirmed that the 40/60 composition gave the best EOPV values during pulse discharge of full size cathodes at 25 A.

Several platinized carbon mixtures were evaluated in an effort to improve the EOPV. The standard 40/60 carbon cathode is compared with the best 40/60

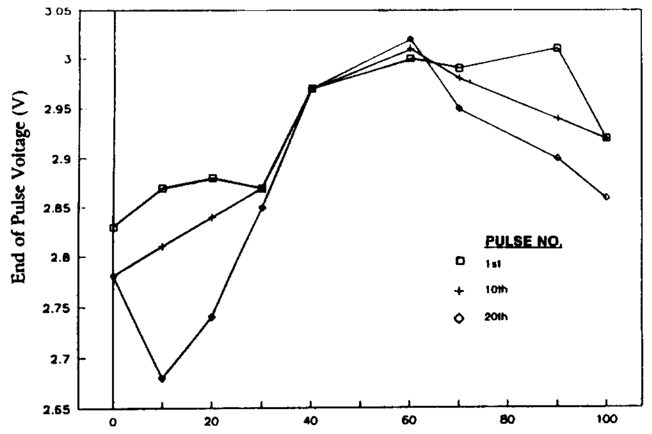

Fig. 3. End-of-pulse-voltage vs. carbon composition, twenty 20 s pulses.

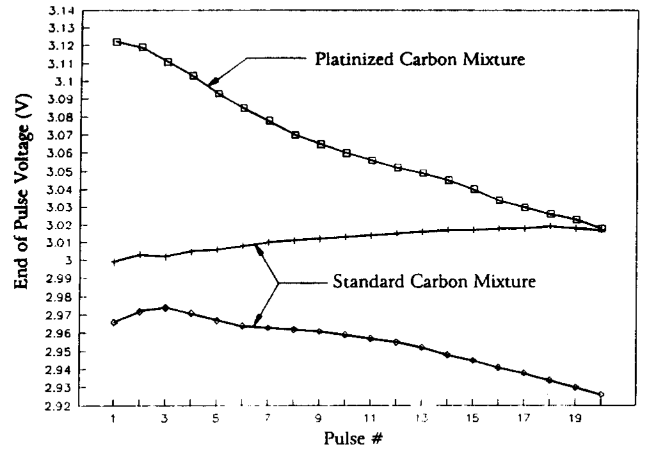

Fig. 4. Comparison of platinized and standard 40/60 carbon cathodes, 20 s pulse discharge at 25 A.

(based on carbon) platinized carbon cathode composition in Fig. 4. One characteristic all platinized cathodes had in common was the initial high EOPV followed by a voltage decrease during each additional pulse. A decrease in the number of catalytic platinum sites leaving only active carbon sites due to poisoning by impurities or blockage by locally deposited LiCl, may explain the observed decrease in cell voltage. The EOPV values for one of the standard cathodes increased slightly, most likely because of a small temperature increase, and reached the same value, 3.02 V, as the platinized carbon cathode during the twentieth pulse. All 40/60 standard carbon cathodes had EOPV values above 2.9 V during evaluation in the special fixture. This standard carbon composition was selected for all further single cell and multicell stack tests.

3.2. Cell design and stack assembly

Cell components are sandwiched between adjacent bipolar plates during stack assembly as shown in Fig. 5. The lithium anode is rolled on to each bipolar plate and anode endplate prior to stack assembly. Preparation of all cell components and stack assembly procedures were performed in a dry room environment with relative humidity less than 2%. To begin assembly, a carbon cathode is centered on the cathode endplate positioned in the assembly fixture. A glass paper separator is then centered over the cathode and the first bipolar plate is positioned over the assembled components, lithium side down. Each additional cell is assembled in like manner starting with the centering of the second cathode on the first bipolar plate. The anode endplate is the last stack component in the assembly procedure. A fill tube is added to each cell for electrolyte activation after stack sealing. The assembled stack components are compressed to the final height in preparation for stack sealing. The Tefzel insulation rings are sealed along the stack periphery except near the fill tubes (initial three-quarters seal). A 330 W iron was used to seal the single cell, 4-cell, and 10-cell stacks initially. Each cell is filled individually with the proper volume of electrolyte from a syringe delivery system. A cathode channel design was developed to help distribute electrolyte throughout each cathode. Stack sealing is completed after activation. Each stack is maintained under external compression after activation and during final sealing in preparation for testing. For fabrication of a single cell using bipolar hardware, cell components are assembled between anode and cathode endplates.

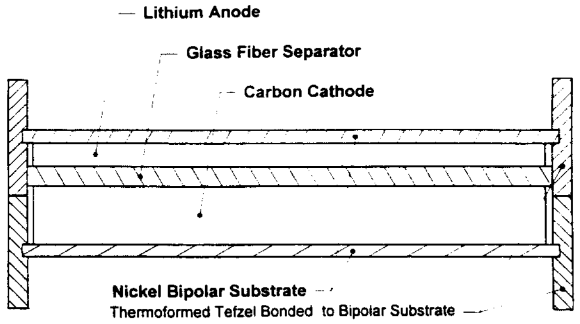

Fig. 5. Single cell components in stack subassembly.

3.3. Single cell tests using stack hardware

Several constant power pulse tests were performed with single cells assembled from stack hardware. The full size 10 in diameter cathode was down-sized to a 9.25 in diameter cathode for the torpedo-size Sonobuoy power source application. Comparison with the full size cathode showed that cell voltage decreased only slightly, i.e., by 50 to 80 mV in going to the smaller diameter cathode. As an example, thirty-one 20 s pulses were obtained during the first constant power continuous pulse discharge test with a 9.25 in cathode. The average

EOPV value in this test was 2.96 V from the second through the twentieth pulse.

3.4. Multicell stack tests

The load voltage in multicell stacks is sensitive to changes in compression on stack components. The external compression was adjusted on several multicell stacks during the initial few pulses in order to maximize stack performance throughout the rest of the test. One characteristic of multicell stacks observed during testing was the increase in voltage, usually during the first 10 to 12 pulses, due to an increase in stack temperature. Twenty-seven pulses were obtained during testing of a 10-cell stack, Fig. 6. The peak voltage, 31.81 V, occurred during pulse 11 for an average of 3.18 V per cell.

A 50-cell engineering stack was built with 10 in electrode components in order to establish a procedure for the assembly, sealing and activation of large stacks. The stack was assembled as described above. Stack components were compressed between 1 in thick lucite support plates using C-clamps prior to initial stack sealing. It is important that the bipolar plate/Tefzel ring cell assemblies are seated properly, i.e., are compressed into a flat configuration of cells that will maintain proper component contact/compression during activation and testing. The bipolar rings form an uneven vertical surface which must be smoothed in order to insure Tefzel/Tefzel bonding among adjacent rings around the periphery of the stack. The initial three-quarters sealing was done with a 550 W iron. One layer of a fiberglass/Tefzel composite was applied to the initial seal in order to thicken and strengthen the Tefzel/Tefzel bonded rings.

Compression was relaxed during electrolyte activation which allowed the stack to expand somewhat in the center, part of the normal activation procedure. The cathode could not be uniformally compressed to a flat configuration after activation because of cathode expansion, and as a result, a change was made in the activation procedure to correct this problem. Fourteen pulses were obtained during pulse discharge, Fig. 7. Twelve pulses occurred at load voltages above 150 V, better than 3 V per cell on average. The maximum voltage, 160.75 V, occurred during the sixth pulse, for an average of 3.21 V per cell.

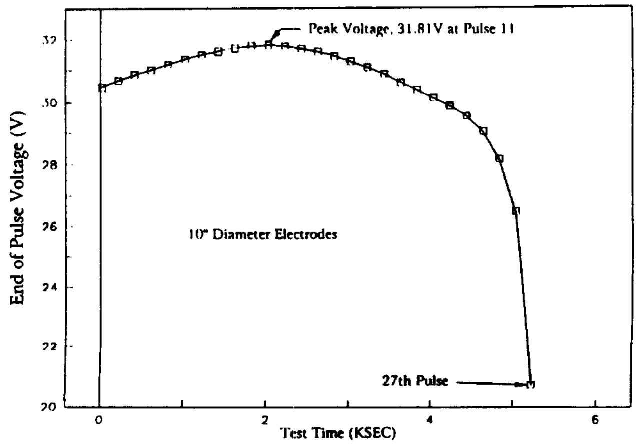

Fig. 6. End-of-pulse-voltage for first 10-cell stack during constant power (714 W) continuous pulse discharge.

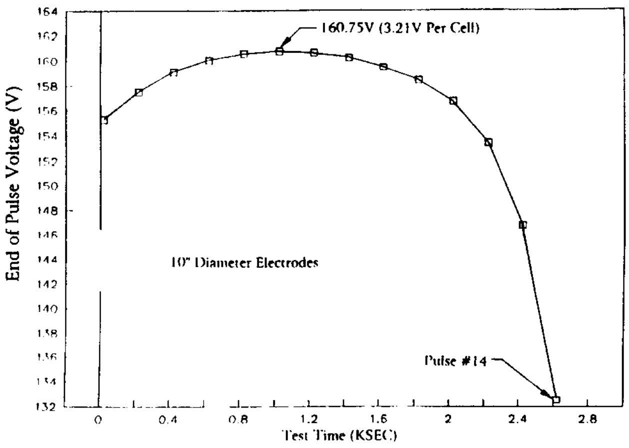

Fig. 7. End-of-pulse-voltage for first 50-cell stack during constant power (3570 W) continuous pulse discharge.

The first 150-cell bipolar configuration was assembled from three 50-cell stacks connected in series with silver plated copper connectors during pulse discharge. Each 50-cell stack was maintained under compression in a 'flat' configuration between 1 in thick lucite disks during the initial three-quarters sealing, electrolyte activation, and final sealing steps. Final compression was supplied with six C-clamps arranged symmetrically around each stack during discharge; three at half the radial distance and three at the periphery. The EOPV values for the 150-cell configuration are plotted in Fig. 8. Several of the initial pulses were less than 20 s in duration because of problems associated with the high voltage instrumentation/software test setup. Current instability developed during pulse 7 (terminated after 15 s) when the power increased to 25.9 kW after 7 s of controlled discharge at 10.7 kW. The 19 partial/complete pulses are equivalent to fourteen 20 s pulses.

The high power discharge during pulse 7 may have contributed to the less than expected number of 10.7 kW pulses. A second reason would be electrolyte leakage. Minimal leakage occurred during activation of individual cells in each stack, but additional electrolyte was loss prior to and during the test from several small leaks that developed between adjacent Tefzel rings in each of the three stacks.

3.5. Assembly and testing of a 150-cell bipolar module

Fabrication and testing of the multicell stacks and problems associated with two 150-cell modules indicated

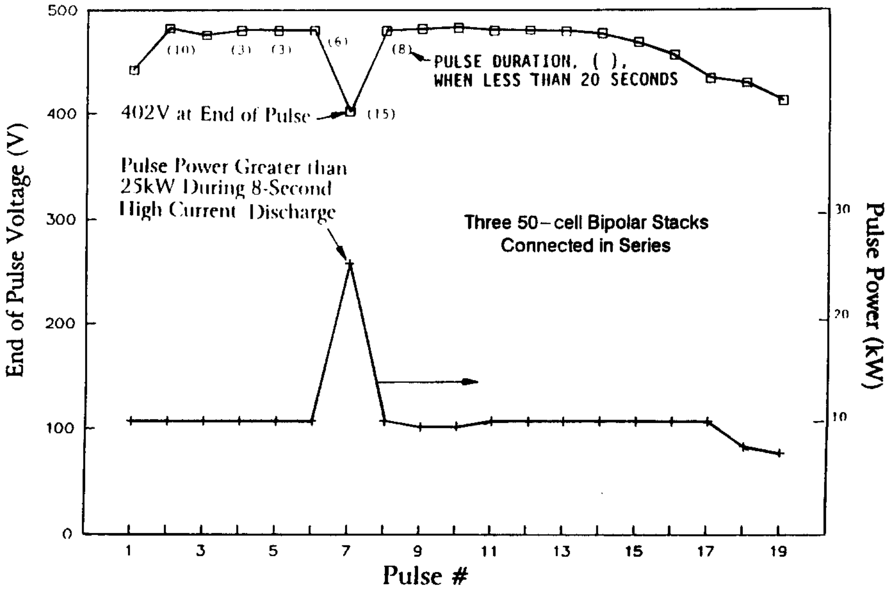

Fig. 8. End-of-pulse-voltage for first 150-cell bipolar configuration of three 50-cell stacks connected in series during constant power (10.7 kW) pulse discharge test.

several problem areas which needed to be addressed: Tefzel stack sealing, cell activation, and the handling of large modules during assembly being the most important. Changes and improvements made in these and other areas are discussed below:

(i) The assembly fixture was redesigned so that a uniform compression could be applied to the stack during assembly. Handling is improved since a large module can be rotated under compression in this fixture for ease of sealing and electrolyte activation.

(ii) The cathode channel design was modified so that the fill tube is no longer compressed between the separator and cathode. This change improved module flatness under compression.

(iii) The quality of the sealed Tefzel surface was improved by replacing the soldering iron 'contact method' with a hot gas welder. This type of welder was observed to melt the Tefzel stack surface without causing extensive degradation of the thermoplastic material.

(iv) A polarization test was developed to monitor the electrochemical condition of a large module prior to the start of testing.

(v) The wicking capability of the cathode was improved by reducing the TFE content of the carbon composition. Several wetting experiments were conducted to compare high and low TFE cathodes. Electrolyte distribution between the cathode and separator components and electrolyte retention by the cathode improved with reduction in the TFE component.

A third 150-cell bipolar module was assembled during a two-day period in the production dry room using low TFE cathodes and incorporating the other changes and improvements discussed above. Every effort was made to minimize exposure of the components and module to moisture during the assembly, initial stack sealing, electrolyte activation, and final sealing steps. Several tabs were TIG welded between the anode and cathode honeycomb support structures to provide compression to the module during testing.

Twelve 20 s pulses were obtained during the 10.7 kW constant power pulse test. The lowest voltage and EOPV values are plotted for each pulse in Fig. 9. Module voltage increased during the first five pulses, then peaked at 498.2. V during the sixth 20 s 10.7 kW pulse. Module voltage started to drop after the seventh pulse. The pulse test was terminated after the twelfth pulse because of the rapid drop off in voltage between the eleventh and twelfth pulses. Recovery of the open-

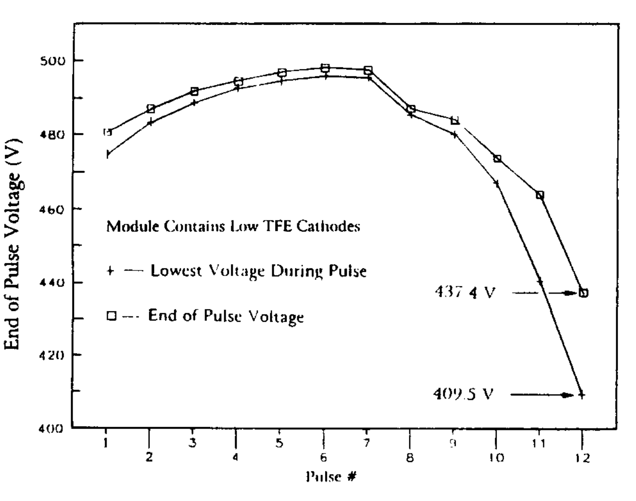

Fig. 9. The lowest voltage and end-of-pulse-voltage for each pulse of the third 150-cell module during the 10.7 kW constant power pulse test.

circuit voltage to 544 V after each pulse was an indication that no internal shorts had occurred. The rapid drop off in module voltage after pulse 7 is evidence that a few cells were weak from lack of an adequate electrolyte content.

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