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RECHARGEABLE LITHIUM CELLS WITH HIGH ENERGY DENSITY TRANSITION METAL COMPOUND CATHODES-CHARACTERIZATION IN AA-SIZE CELLS

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PREFACE

This report addresses the development and testing of 0.85-Ah Li/Li_xCoO₂ cells. The effort allowed for a direct correlation between Li_xCoO₂ and other cathodes for lithium batteries which were evaluated under an outgoing testing program by the High Energy Battery Project, Naval Surface Warfare Center, Dahlgren Division, White Oak Detachment (NSWCDDWODET) under the leadership of Dr. Patricia H. Smith. This work was performed under Contract N60921-89-D-0039.

Two previous reports, <u>Development of a 30-Ampere-Hour Lithium/lithium Cobalt Oxide</u> <u>Rechargeable Battery</u>, NAVSWC TR 91-184 and <u>Silver Oxide/Zinc Rechargeable Cells-A Comparison</u> <u>with High Energy Density Lithium/Lithium Cobalt Oxide</u>, CARDIVNSWC-TR/027, detailed the development activities and performance evaluations on lithium/lithium cobalt oxide (Li/Li_xCoO₂) cells of sizes 7- to 30-ampere-hour (Ah).

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CHAPTER 1

INTRODUCTION

The range of underwater vehicles powered by batteries is limited by the energy density (watthours per pound, Wh/lb) that can be delivered by the battery type at the power density (watts per pound, W/lb) at which that capacity is delivered. Larger underwater vehicles (submarines) have been battery powered since the late 19th century. Lead-acid batteries are generally used because they provide many cycles but at low energy density. Smaller underwater vehicles are usually powered by silver oxide-zinc (AgO/Zn) batteries. These offer three times the energy density of lead-acid.¹ The vehicle range is thereby increased, but a severe reduction in cycle life must be accepted.

BACKGROUND

Office of Naval Research and the former Office of Naval Technology have funded batteries based on more energetic couples, such as lithium/lithium cobalt dioxide (Li/Li_xCoO₂), to replace the AgO/Zn batteries now used to propel Swimmer Delivery Vehicles (SDVs) and other submersibles. The design goal is to deliver a minimum energy density of 100 Wh/lb for at least fifty cycles at any seawater temperature (-2°C to +35°C) and for the battery to last five years in storage.

Three activities were conducted as part of this development. They are reported in separate reports. The principal activity led to the development and evaluation of 7- to 30-Ah cells.² Another activity investigated the performance of 30-Ah AgO/Zn cells³ for comparison to Li/Li_xCoO₂. The third activity, which is the subject of this report, embodied the system in cells of 0.85-Ah capacity using cases with dimensions of the American Standards Association (ASA) Size AA. The use of the AA size as a test vehicle, to complement the work in the larger sizes, was prompted by several considerations. An ongoing study at NSWC has been comparing the performance of different lithium chemistries in that size, maintaining comparable cathodic current densities.^{4,5} Data from the present work have been incorporated into that ongoing study and published in part.^{6,7}

Another reason for using the AA-size cells was that it provided a sealed cell in a readilyfabricated embodiment. These cells were used to assess performance on deeper discharges and more abusive conditions than employed in the other studies.

Finally, one proposed design element replaced the conventional glass-to-metal (GTM) seal (between the terminals and the case) by a compression seal. This substitution could be tested in smaller cells, such as the AA size, because such seals were commercially available. By contrast, some development would have been required to design a compression seal for larger cells.

Earlier NSWC work⁸⁻¹⁰ on the Li/Li_xCoO₂ system demonstrated its unique characteristics: high energy, high cell voltage, excellent rate capability, and good reversibility. These studies defined the baseline system.

The cell discharge reaction is given by Equation 1-1:

$$(1-x)Li + Li_{x}CoO_{2} \rightarrow Li_{1,0}CoO_{2}$$
(1-1)

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in which, since one electron is transferred, one Faraday per mole (1 F/M) is delivered when x is zero. On charge, the reverse reaction occurs. However, it is known that the range of values that x can assume is limited for practical rechargeable Li/Li_xCoO₂ cells.¹¹ Mizushima *et al.* showed that the limited voltage range was dictated by structural changes in the crystal lattice.¹² Nevertheless, these workers also showed¹² that lithium could be removed reversibly down to at least x = 0.067. The range, within which a useful number of cycles may be attained, has been identified to be between 3.0 to 4.3 volts (V), which corresponds to cycling between the compositions Li_{1.0}CoO₂ and Li_{0.5}CoO₂.^{2,11}

CHAPTER 2

EXPERIMENTAL

The materials and processes used to prepare the AA-size cells are described in this chapter. The test matrix is presented as well as the rationale for the entries therein, including the reasons for discharging some cells to achieve greater utilizations than are generally demanded of the system.

MATERIALS

Electrolytes and Electrodes

Electrolyte Solutions. The following electrolyte components were used as received:

- lithium hexafluoroarsenate (LiAsF₆), Electrochemical, LaRoche;
- carbon dioxide (CO₂), Bone Dry, Toll Co.; and
- methyl formate (HCOOCH₃), Alliant Techsystems' specification, E. M. Science.

Lithium tetrafluoroborate (LiBF₄), Electrochemical, Cyprus Foote Mineral Co., was dried at 80° C under vacuum (200 millitorr) for 16 hours, minimum.

Solutions were prepared in a glove box under argon. $LiAsF_6$ and $LiBF_4$ were dissolved in methyl formate to obtain concentrations 2.0 molar (*M*) in $LiAsF_6$ and 0.4 *M* in $LiBF_4$. The solutions were then saturated with CO₂ by passing the gas through them at a pressure of 30 pounds per square inch, gage (psig) for at least 30 minutes. Typically, they had less than 50 parts per million (ppm) of water, as measured by a Photovolt Model 128 Fischer Titrator.

<u>Anode</u>. Lithium (Li, 99.9% minimum) Cyprus Foote Mineral Co., was purchased in 0.008-inch (") thickness and used as received.

Cathode Components. Used as received were:

 lithium cobalt dioxide (LiCoO₂), Alfa Catalog; or, lithium cobalt (III) oxide, (LiCoO₂), Johnson Matthey;

• carbon (C) Cabot Corp, type Vulcan XC-72R (98.5%), (characterized by a surface area of 254 square meters per gram (m²/g) and a particle size of 30 microns); and

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• polytetrafluoroethylene ($[-CF_2CF_2-]_n$), DuPont Corp., Teflon-30, (an aqueous emulsion, 60% solids).

Separators.

Microporous, high density polyethylene separators, 3M Co., type E003, were dried under vacuum (200 millitorr) at room temperature for a minimum of 16 hours prior to use. In most of the cells, four layers of this separator were used between the anode and cathode plates. In the text, this separation system is identified as "engineering baseline."

In some cells, one layer of a special separator, Hoechst Celanese Corp. Celgard type K-613, was sandwiched between two layers of the E003 separator. The Celgard separator is designed to create a high electrical resistance in the event of a temperature rise, such as may be caused by a short circuit. The resistance is due to separator melting. This separation system will be identified as "experimental shutdown" in the text. The physical properties of the separators are listed in Table 2-1.

Inert Metal Components

Metal parts were washed with deionized water (H_2O) followed by ultrasonic cleaning in a commercial degreasing solution (Allied Signal Corporation's Genesolv DES, composition by weight, 93.5% trichlorotrifluoroethane, 3.5% ethanol, 2% isopropanol, 1% nitromethane and a trace of methanol). The cleaned parts were then vacuum dried at 200 millitorr and 125°C for a minimum of 16 hours prior to use.

<u>Current Collectors.</u> Current collectors for both the anode and cathode were made of expanded metal: aluminum for cathodes, nickel for anodes, Exmet Corporation's type 5Al8-4/0 and 3Ni5-3/0A, respectively. Tabs of the same metal as each collector were welded on as electrical leads. The anode collector was cut to 1.45-in. x 4.5-in.; the cathode collector, to 1.43-in. x 4.0-in.

<u>Cell Cases.</u> Cylindrical cell cases were fabricated by Hudson Tool & Die Corp. from type 304 stainless steel (SS). They were American Standards Association Size AA (0.53-in. diameter and 1.88-in. height). The base of the case was coined to provide a structurally weak region that allowed the cell to vent if the internal pressure reached 600 ± 325 psig.

<u>Headers.</u> Case headers were of type 304 SS. As mentioned above, the GTM seal generally used to isolate one terminal from the header was not employed. A compression seal was used instead. Compression seals have been shown to be very effective when properly designed.¹³ A drawing of the seal is shown in Figure 2-1. They were designed and provided by Three E Laboratories, Inc. The insulating material between the aluminum positive terminal and the header was ethylenechlorotrifluoroethylene copolymer (ECTFE), "Halar." Three crimps were applied to ensure the seal, as shown in the figure. The seals were designed to withstand at least 2,000 psig.

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PROCESSES

Cathode Processing

<u>Cathode Mix</u>. A dry mixture of $LiCoO_2$ and C (90:10 weight ratio) was mulled in a Simpson mix-muller (National Engineering Company, Chicago, Illinois) for 70 minutes. Separately, 16 g of Teflon-30 were blended with 300 milliliters (mL) H₂O. Half of the diluted Teflon dispersion was added to 280 g of the mulled dry mix and blended for 60 seconds. Then the rest of the Teflon dispersion was added and blending was continued for another 10 minutes. After filtering, the cake was kneaded in a polyethylene bag until it developed a clay-like consistency. The final composition was LiCoO₂/carbon/polytetrafluoroethylene, in the ratio: 87/9.67/3.33, respectively.

<u>Cathode Pad Formation</u>. Cathode pads were made by passing the kneaded cathode mix through a roll mill six times at a gap setting of 0.080 inches. After every two passes, the pad was folded in half and rotated 90 degrees. This procedure was repeated three times, except that the roller gap setting was reduced 0.020 inches every six passes until a final setting of 0.020 inches was reached.

<u>Cathode Pad/Collector Formation.</u> Cathode pads were rolled onto the expanded metal collectors at a gap setting of 0.020 inches followed by drying at 200°C for at least 16 hours. The composite was then passed through the roller at the same setting once while it was still warm to smooth the surface. Pad dimensions exceeded those of the 4-in. x 1.43-in. current collector, but were trimmed after drying. The final cathode dimensions were 1.45-in. x 3.2-in. x 0.022-in. Finished cathodes were vacuum dried at 170°C for a minimum of 16 hours prior to use.

Anode Processing

Lithium foil, 0.008-in. thick, was cut to 1.5-in. x 4.5-in. for pressing on each side of the 1.45-in. x 4.5-in. current collector by rolling. First, one piece of lithium was rolled onto one side of the collector. Then a second piece was rolled onto the opposite side. A portion of the lithium flowed into the openings in the expanded metal; the final anode thickness was 0.015 inches.

CELL CONSTRUCTION

The cell design was not optimized. Therefore, the cells built and tested should not be considered prototypes. Electrodes were of a rolled configuration. A sketch of the plates and the electrical leads is given in Figure 2-2. Cells were hermetically sealed by welding. A total of 63 cells were built. Each weighed approximately 16.25 g. Cell capacity was limited by the mass of active material in the cathode. Discharge capacity based on complete utilization (from x = 0 to x = 1 in Li_xCoO₂) would provide 0.85 Ah.

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TESTING

Cycle Testing

A cycling test regime was used which, in some cases, pushed the recognized limits of the system. Other tests were used to assess charge retention over long storage periods, to evaluate the performance of the compression seal, and to measure cell behavior during the abuses of thermal cycling, excessive heating, and shorting. The test matrix is shown in Table 2-2.

<u>Discharge/Charge Limits for Li/Li_xCoO₂</u>. The cycling of Li/Li_xCoO₂ cells is generally within a limited range of x. Assuming that range to be $0.5 \le x \le 1.0$, discharge through it usually is considered 100% DOD. In this study, however, the <u>unusual</u> practice was assumed of cycling over a larger range, and 100% DOD corresponds to x over the range of $0 \le x \le 1$, or a utilization of 1 F/M.

To deliver a subsequent discharge at 75% DOD (0.75 F/M), cells were initially charged to oxidize the $LiCoO_2$ to $Li_{0.25}CoO_2$, and then cycled as described below. For the 50% DOD, the cells were charged to $Li_{0.5}CoO_2$, and for the 37.5% DOD, to $Li_{0.625}CoO_2$. The 75% DOD allowed correlation with AA-size lithium cells of other chemistries,⁴⁻⁷ but also tested Li/Li_xCoO_2 under conditions not recommended for the system. The reason for the inclusion of cells discharged at 37.5% DOD was to examine the effect of a low DOD. For many rechargeable battery systems, cycle life increases as the DOD decreases. Selecting these three depths of discharge would enable evaluation of cycle life as a function of depth of discharge over a wide range. The inclusion of testing at -2°C, at the lowest depth of discharge, was to provide a point of comparison to some 7- to 30-Ah cells cycled at that temperature but at 50% DOD.

The rest of the cells in the test matrix were cycled using a regime to directly compare the Li/Li_xCoO_2 system to lithium cells using other cathodes in AA-size cells.⁴⁻⁷ For that reason, the test matrix consisted of the three specific discharge rates: 1, 5, and 10 mA/cm² (based on total cathode area); two depths of discharge, 50% and 75%; and two cycling temperatures, 0°C and 25°C. Charging was consistently at 0.5 mA/cm².

For each condition, the average of the cell voltages at the end of the initial coulometric charge (ampere-hours into the cell) and the average of the voltages at the end of the initial coulometric discharge (ampere-hours out of the cell) were selected as the cutoff voltages for subsequent cycling, if the charge or discharge was not first terminated coulometrically. By using this method of determining voltage cutoffs, the fresh Li/Li_xCoO₂ cells were charged and discharged beyond the recommended voltage range 3.0-4.3 V. For example, at 50% DOD, cells discharged at 5.0 mA/cm² and 0 °C were cycled between 4.23 and 0.78 V. At 10 mA/cm², they were cycled between 4.22 and 0.63 V. For the 75% DOD, the average cutoff voltage on charge was as high as 4.65 V. When the charge could not accept the desired number of coulombs because it was terminated by the charge cutoff voltage, the capacity delivered on the subsequent discharge was correspondingly reduced.

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Storage Testing

As shown in Table 2-2, some cells were charged to 4.1 V and put into storage to evaluate selfdischarge over six months.

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FIGURE 2-1 CASE HEADER FOR AA-SIZE CELL SHOWING COMPRESSION SEAL



 \triangle Separator must project beyond electrode edges at any point along spiral

FIGURE 2-2. AA CELL WRAP

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TABLE 2-1 PHYSICAL PROPERTIES OF SEPARATORS					
	E003	K-613			
Material Type	High Density Polyethylene	Polypropylene			
Thickness (inch)	0.0012	0.003			
Porosity (%)	60	38			
Pore Size (micron)	0.09	0.05 x 0.125			
Melt Temperature (°C)	125				

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TABLE 2-2. AA-SIZE CELL TEST MATRIX							
	NO. OF CELLS						
Temp., °C	DOD, %(1)	Discharge Rate mA/cm ²	Others	Base-line Separator	Shut- down Separator		
25	75	1 5 10		3 3 3	2 2 		
	50	1 5 10		3 3 3	2 2 		
0	75	1 5 10		3 3 3	1 		
	50	1 5 10	c	3 3 3	1 		
25	37.5	5		2	1		
-2		5		2 (6)	1		
25	50	1 1 1	1 mo. storage after 1 charge to 4.1 V 3 mos. storage after 1 charge to 4.1 V 6 mos. storage after 1 charge (2) to 4.1 V	1 2 2			
	l Safety Tes	lsts	thermally cycled(3) heat mode (4) short-circuit (5)	1 1 1	.1 1 1		

Notes:

(1) DOD is based on 1 Faraday/Mole.

- (2) Actually, one cell discharged after 7 months, one after 9 months.
- (3) Cells were thermally cycled between -20 °C and 40 °C, 2 hours for each temperature. Total cycle time was 2 days.
- (4) After 6th charge to 4.2 V, cells were heated to 50 °C for 2 hours then increased every 30 °C and stayed at that temperature for 2 hours until cells vented.
- (5) Cells received 1st charge to 4.3 V prior to this test.
- (6) One cell was thermally cycled per condition (3) prior to cycling test.

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CHAPTER 3

RESULTS AND DISCUSSION

The results of testing on fresh cells are discussed in terms of discharge rate and temperature. Capacity loss during storage is also presented.

FRESH CELL PERFORMANCE

Table 3-1 details the cycle life results for fresh cells. In general, reproducible performances were obtained at the discharge rates of 1, 5, and 10 mA/cm², at the stated depths of discharge and temperature. Complete data are presented in the table. For clarity, data for one cell, typical of the group, are plotted in the figures.

Capacity at room temperature, as a function of the number of cycles for all three rates, is plotted in Figure 3-1 and Figure 3-2 for 75% and 50% DOD's, respectively. Capacity at 0°C, as a function of the number of cycles for all three rates, is plotted in Figure 3-3 and Figure 3-4 for 75% and 50% DOD's, respectively. While at both temperatures and the lowest rates, 40 to 50 cycles were obtained for the cell cycled to 50% DOD, only about half that number were obtained at 75% DOD. The 50% DOD results are in general agreement with cycling data for 7- to 30-Ah cells at the same depth of discharge. The larger cells, however, were typically cycled at 1.6 mA/cm² (cathode). The AA-size cell's performance was relatively independent of temperature, as was that of the larger cells. To illustrate this more clearly, Figures 3-5 and 3-6 present data for the discharges at 1 and 10 mA/cm², respectively, in which two DOD's and two temperatures are superimposed.

The cells cycled at 37.5% DOD with the two different separators gave interesting data; plots of capacity vs. cycle number are presented in Figure 3-7. While only a limited number of cells were tested and plotted, introducing some caution to any conclusions, the first observation is that the experimental shutdown separator hurt cycle life. Another observation may be more important. At the reduced depth of discharge, cell performance is quite dependent on the temperature. The cycles life at 22°C greatly exceeded that at -2°C. This contrasts to prior data that show an independence of performance with temperature over the range -2 to 35°C.^{2,3} The increase in cycle life with lower depth of discharge, observed for the 75% and 50% DOD test was also seen at the lowest depth of discharge. The cell of the same construction as those plotted for 50% DOD in Figure 3-2, at 35% DOD, demonstrated over twice the number of cycles.

Cells cycled at 75% DOD displayed capacity fading attributed to structural instability and/or

solvent oxidation. Surprisingly, however, these cells can be abusively cycled without displaying abrupt performance deterioration.

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CELL PERFORMANCE AFTER STORAGE

Six cells were put on extended storage for up to nine months at 22°C after being charged once to 4.1 V. The initial charge capacities and the measured discharge capacities are presented in Table 3-2. The capacity fell off 9% after one month storage. After a capacity loss of about 13% by the third month, no additional loss occurred up to nine months. The capacity loss was recovered almost 100% on subsequent cycling, see Figure 3-8. The voltage dips in the plots are attributed to intermittent shorts. As previously mentioned, the cell design was the first attempt to embody the system in a AAsize cell, and design improvements would be expected to significantly reduce the occurrence of shorting.

CELL SAFETY EVALUATIONS

Safety evaluations included thermal cycling, excessive heating, and short circuiting. Two cells were thermally cycled between -20°C and +40°C over two days. The cells were held at least two hours at each temperature. Visible checks showed excellent seal integrity and no measurable weight loss.

An experiment was performed to evaluate the experimental shutdown separator. Two cells were tested. One was constructed with the baseline separator and the other with the experimental shutdown separator. The cells were fully charged after being cycled five times and then heated by manually adjusting the applied temperature to values and at the times shown in Figure 3-9 for the cell with the experimental shutdown separator and in Figure 3-10 for the baseline. Cell voltages were simultaneously recorded, and these are also plotted in the figures. At about 110°C, both cells exhibited abrupt shorting followed by venting through the coin. The ventings did not produce a lithium fire, and the compression seal remained intact. Venting is ascribed to the decomposition of methyl formate. Thus, in this test, cell performance was independent of separator, and cell performance was not terminated by separator shutdown.

Two cells, one constructed with the baseline separator, the other with the experimental shutdown separator, were given a full charge before they were short circuited. Plots of the case temperatures and cell currents as a function of time are shown in Figure 3-11. Both cells registered a peak current at about 20 A (equivalent to 328 mA/cm²), and the case temperatures did not rise more than 94°C. The two cells remained intact during the tests, and the separator did not shut down.



FIGURE 3-1. CAPACITY OF AA-SIZE CELLS AT 75% DEPTH OF DISCHARGE VS. CYCLE NUMBER, 22°C, CURRENT DENSITIES: 1, 5, AND 10 mA/cm²



FIGURE 3-2. CAPACITY OF AA-SIZE CELLS AT 50% DEPTH OF DISCHARGE VS. CYCLE NUMBER, 22°C, CURRENT DENSITIES: 1, 5, AND 10 mA/cm²



FIGURE 3-3. CAPACITY OF AA-SIZE CELLS AT 75% DEPTH OF DISCHARGE VS. CYCLE NUMBER, 0°C, CURRENT DENSITIES: 1, 5, AND 10 mA/cm²



FIGURE 3-4. CAPACITY OF AA-SIZE CELLS AT 50% DEPTH OF DISCHARGE VS. CYCLE NUMBER, 0°C, CURRENT DENSITIES: 1, 5, AND 10 mA/cm²

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FIGURE 3-5. EFFECT OF DEPTH OF DISCHARGE (50 OR 75%) AND TEMPERATURE (0 OR 22°C) ON CAPACITY OF AA-SIZE CELLS VS. CYCLE NUMBER, CURRENT DENSITY 1 mA/cm²



FIGURE 3-6. EFFECT OF DEPTH OF DISCHARGE (50 OR 75%) AND TEMPERATURE (0 OR 22°C) ON CAPACITY OF AA-SIZE CELLS VS. CYCLE NUMBER, CURRENT DENSITY 10 mA/cm²



FIGURE 3-7. CAPACITY AT 37.5% DEPTH OF DISCHARGE VS. CYCLE NUMBER FOR AA-SIZE CELLS WITH BASELINE OR EXPERIMENTAL SHUTDOWN SEPARATORS AT 0 AND 22°C



FIGURE 3-8. CAPACITY VS. CYCLE NUMBER FOR CELLS WHICH WERE CHARGED TO 4.1 V PRIOR TO ROOM TEMPERATURE STORAGE, THEN DISCHARGED AT 1 mA/cm² AFTER 1, 3, 7, OR 9 MONTHS

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FIGURE 3-9. EFFECT OF APPLIED HEAT ON AA-SIZE CELL WITH EXPERIMENTAL SHUTDOWN SEPARATOR; CELL TEMPERATURE AND CELL VOLTAGE VS. TIME; SHORTING FOLLOWED BY VENTING, ABOUT 110°C



FIGURE 3-10. EFFECT OF APPLIED HEAT ON AA-SIZE CELL WITH BASELINE SEPARATOR; CELL TEMPERATURE AND CELL VOLTAGE VS. TIME; SHORTING FOLLOWED BY VENTING, ABOUT 110°C

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FIGURE 3-11. SHORT CIRCUIT CURRENT AND CELL TEMPERATURE VS. TIME, TWO AA-SIZE CELLS

TABLE 3-1. PERFORMANCE OF AA-SIZE LI/LI,CoO, CELLS													
NOMINAL CELL CAPACITY: 0.85 Ah (based on 1 F/M of LiCoO ₂ CELL WEIGHT: 16.247 g													
Test Cond.	Cell No.	Cycle No.	Cap. F/M	Avg. Volt	Wh/lb	Cycle No.	Cap. F/M	Avg. Volt	Wh/ib	Cycle No. †	Cap. F/M	Avg. Volt	Wh/lb
					TEN	IPERATU	<u>RE = R/</u>	r					
75% DOD 1 mA/cm²	H23 H35 H45 Avg.	1 1 1	0.751 0.751 0.751 0.751 0.751	3.67 3.76 3.79 3.74	65.46 67.07 67.61 66.71	14 14 13** 14	0.484 0.524 0.355 0.504	3.16 3.16 3.15 3.16	36.33 39.33 26.56 34.07	28** 28 28	0.413 0.234 0.324	2.85 2.62 2.74	27.96 14.56 21.26
	H67* H74* Avg.	1 1 1	0.750 0.751 0.751	3.69 3.58 3.64	65.73 63.86 64.80	14 14 14	0.478 0.523 0.501	2.99 3.12 3.06	33.95 38.76 36.35	22 35 29	0.268 0.332 0.300	2.98 2.89 2.94	18.97 22.79 20.88
75% DOD 5 mA/cm ²	H36 H42 H44 Avg.	1 1 1	0.715 0.746 0.754 0.738	2.84 3.42 3.38 3.21	48.23 60.60 60.53 56.45	20 20 20 20 20	0.505 0.485 0.390 0.460	2.30 2.44 2.30 2.35	27.59 28.11 21.31 25.67	41 28 34** 34	0.214 0.390 0.201 0.268	2.16 2.00 1.85 2.00	10.98 18.53 8.83 12.78
	H73* H76* Avg.	1 1 1	0.722 0.710 0.716	3.05 2.69 2.87	52.30 45.36 48.83	33 33 33	0.430 0.405 0.418	2.04 1.84 1.94	20.84 17.70 19.27	60 72 66	0.189 0.220 0.205	1.70 2.12 1.91	7.63 11.08 9.35
75% DOD 10 mA/cm ²	H20 H27 H38 Avg.	1 1 1	0.680 0.680 0.687 0.682	2.75 2.80 2.45 2.67	44.42 45.22 39.98 43.21	13 13 13 13	0.544 0.481 0.467 0.513	2.27 1.70 2.10 1.99	29.33 19.42 23.29 24.38	29 22 22 24	0.332 0.298 0.261 0.280	1.67 1.54 1.56 1.55	13.17 10.90 9.67 10.29
50% DOD 1 mA/cm ²	H25 H37 H41 Avg.	1 1 1	0.499 0.500 0.500 0.500	3.72 3.68 3.85 3.75	44.09 43.70 45.72 44.51	24 24 24 24 24	0.435 0.410 0.455 0.433	3.53 3.48 3.51 3.51	36.47 33.89 37.93 36.10	45** 52 45 47	0.281 0.157 0.272 0.215	3.28 3.04 3.24 3.19	21.89 11.34 20.93 18.05
	H66* H68* Avg.	1 1 1	0.501 0.501 0.501	3.70 3.72 3.71	44.03 44.27 44.15	24 24 24	0.427 0.414 0.421	3.52 3.52 3.52	35.70 34.61 35.16	46 47 47	0.146 0.147 0.147	2.95 2.94 2.95	10.23 10.27 10.25
50% DOD 5 mA/cm²	H26 H29 H40 Avg.	1 1 1	0.506 0.507 0.506 0.506	3.29 3.00 3.41 3.23	39.54 36.13 40.98 38.88	24 24 24 24 24	0.443 0.419 0.385 0.402	2.80 2.76 2.48 2.68	29.46 27.47 22.68 26.54	48** 48 29** 42	0.226 0.138 0.288 0.213	2.00 2.28 2.32 2.20	10.74 7.47 15.87 11.36
	H69* H71* Avg.	1 1 1	0.532 0.501 0.517	3.09 3.09 3.09	39.05 36.77 37.91	28 28 28	0.405 0.405 0.405	2.30 2.55 2.43	22.13 24.53 23.33	59 54 57	0.131 0.167 0.149	1.81 1.66 1.74	5.65 6.58 6.11
50% DOD 10 mA/cm ²	H22 H49 H64 Avg.	1 1 1	0.500 0.490 0.508 0.499	3.30 2.84 2.63 2.92	39.19 33.05 31.73 34.66	20 20 20 20	0.140 0.412 0.426 0.326	2.31 2.38 2.33 2.34	7.68 23.29 23.58 18.18	 55 40 48	 0.412 0.426 0.419	 2.38. 2.33 2.36	 23.29 23.58 23.43
37.5% DOD 5 mA/cm²	H02 H03 Avg.	1 1 1	0.310 0.370 0.340	3.68 3.71 3.70	27.10 32.60 29.85	60 60 60	0.385 0.369 0.377	3.51 3.62 3.57	32.10 31.73 31.91	117 117 117	0.095 0.138 0.117	3.45 3.41 3.43	7.78 11.18 9.48
I	H07*	1	0.372	3.72	32.87	35	0.360	3.63 Tal	31.04	70 sonthe	0.119	3.48 page.	9.84

Table continues on the following page.

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NOMINAL C		ACITY: 0	.85 Ah (ba	ised on 1	F/M of LiCo	00 ₂)							
Test	Cell	Cycle No.	Cap. F/M	Avg. Volt	Wh/lb	Cycle No.	Cap. F/M	Avg. Volt	Wh/lb	Cycle No.	Cap. F/M	Avg. Volt	Wh/I
<u> </u>			·		TEM	PERATU	RE = 0 *0	5					_
75% DOD 1 mA/cm²	H57 H60 H61 Avg.	1 1 1	0.750 0.750 0.742 0.747	3.83 3.86 3.10 3.60	68.23 68.76 54.63 63.87	12 12 12 12 12	0.537 0.213 0.518 0.423	2.78 2.97 2.87 2.87	35.46 15.03 35.31 28.60	31 	0.216 0.389 0.303	2.49 2.87 2.68	12.77 26.52 19.65
	H70*	1	0.750	3.76	66.98	16	0.536	3.07	39.08	32	0.217	2.78	14.33
75% DOD 5 mA/cm ²	H50 H58 H62 Ava.	1 1 1	0.680 0.755 0.705 0.713	3.00 3.45 3.22 3.22	48.45 61.87 53.92 54.75	21 21 21 21	0.504 0.402 0.495 0.467	2.28 2.51 2.19 2.33	27.29 23.97 25.75 25.67	42 26** 41 36	0.188 0.339 0.190 0.239	2.27 2.36 2.23 2.29	10.14 19.00 10.06 13.07
75% DOD 10 mA/cm²	H43 H48 H52 Avg.	1 1 1	0.732 0.691 0.720 0.714	3.22 3.07 2.92 3.07	55.98 50.39 49.94 52.10	15 15 15 15	0.519 0.225 0.533 0.426	2.27 1.86 2.26 2.13	27.98 9.94 28.61 22.18	33 31 32	0.190 0.282 0.236	1.68 1.53 1.61	7.58 10.25 8.91
50% DOD 1 mA/cm ²	H59 H63 H65 Avg.	1 1 1 1	0.501 0.501 0.500 0.501	3.71 3.71 3.47 3.63	44.15 44.15 41.21 43.17	25 25 25 25 25	0.442 0.452 0.387 0.427	3.49 3.39 3.32 3.40	36.64 36.39 30.52 34.52	42 52 54 49	0.131 0.131 0.142 0.135	3.01 2.75 2.97 2.91	9.37 8.56 10.02 9.31
	H77*	1	0.500	3.78	44.89	29	0.429	3.53	35.97	58	0.131	3.08	9.58
50% DOD 5 mA/cm ²	H51 H53 H54 Avg	1 1 1 1	0.491 0.497 0.487 0.482	2.87 2.90 3.04 2.94	33.47 34.23 35.16 34.29	28 28 28 28 28	0.428 0.425 0.372 0.408	2.55 2.35 2.20 2.37	25.92 23.72 19.44 23.03	70 54 55 60	0.127 0.135 0.125 0.129	2.12 1.88 1.75 1.92	6.40 6.03 5.20 5.87
50% DOD 10 mA/cm²	H30 H55 H56	1 1 1	0.491 0.497 0.487 0.492	2.87 2.90 3.04 2.94	33.47 34.23 35.16 34.29	19 19 19 19	0.352 0.397 0.381 0.377	2.25 1.91 2.20 2.12	18.81 18.01 19.91 18.91	42 36 35 38	0.161 0.182 0.158 0.167	1.84 1.97 1.46 1.76	7.04 8.52 5.48 7.01
	<u>II ~'9</u>	<u>n '</u>	1 0.432		TENA		F = -2°C	t					
37.5% DOD 5 mA/cm ²	H01 H05 Avg.	1 1 1	0.356 0.372 0.364	3.61 3.71 3.66	30.53 32.78 31.65	22 22 22	0.350 0.268 0.309	3.57 3.49 3.53	29.68 22.22 25.95	45 39 42	0.111 0.114 0.113	3.35 3.42 3.39	8.83 9.26 9.05
	H10*	1	0.368	3.48	30.42	26	0.166	3.48	13.72	52	0.101	3.40	8.16

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Indicates cells with experimental shutdown separator.
 This column lists last discharge before capacity fell to 25 % of initial except for entries marked with double asterisk (**).
 Entries were terminated at the indicated discharge because the monitored voltages showed indications of internal cell shorting.
 Cell H01 was pretreated by thermally cycling between -2 °C and 40 °C for two days.

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TABLE 3-2. INITIAL CAPACITY LOSS OF CHARGED AA-SIZE CELLS AFTER STORAGE AT 22 °C						
Storage Time, Months	Charged Capacity prior to Storage, F/M	Delivered Discharge Capacity after Storage, F/M	Capacity Loss, Per Cent			
1	0.354	0.324	8.5			
1	0.468	0.425	9.2			
3	0.415	0.368	11.3			
3	0.422	0.363	14.0			
7	0.381	0.328	14.0			
9	0.385	0.340	12.0			

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CHAPTER 4

SUMMARY AND CONCLUSIONS

Lithium cells with $\text{Li}_x \text{CoO}_2$ cathodes were cycled through the stoichiometric range $0.25 \le x \le 1$. Repeated cycling in the greatest range, however, resulted in a rapid drop in capacity with cycling, presumably due to a rearrangement of the crystal structure and/or solvent oxidation. Nevertheless, and unexpectedly, useful capacities (above 50 percent of initial) for those cells were obtained over about twenty cycles.

For fresh cells, at a given depth of discharge, delivered capacity was relatively independent of cathodic current densities from 1 to 10 mA/cm^2 and over the temperature range -2 to 22 °C. Cycle life decreased as depth of discharge increased. Data for cells cycled at 37.5% depth of discharge, however, suggest that performance may vary with temperature at lower utilizations.

Thermal cycling and cell shorting tests did not evoke any safety concerns. Cells heated to 110°C vented through the safety coin because of the vapor pressure of the solvent. The potential benefit for the use of the shutdown separator could not be confirmed by the tests performed.

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