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Low-cost, lightweight rechargeable lithium ion batteries

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Abstract

The performance of a low cost, prismatic Li-ion rechargeable battery technology based on the $LiMn_2O_4/C$ cell chemistry is described and compared to a cylindrical $LiCoO_2/C$ cell. The $LiMn_2O_4/C$ cell has demonstrated constant current charge, discharge and pulse discharge rate capability comparable to the more expensive $LiCoO_2/C$ technology. For simulated high power radio operation, the high power $LiMn_2O_4/C$ cell offers performance comparable to the commercial $LiCoO_2/C$ cell. The cycle life demonstrated to date of the $LiMn_2O_4/C$ cell, while adequate for military application, is shorter than the $LiCoO_2/C$ cell.

Keywords: Battery; Lithium-ion; Prismatic; Lightweight; Performance; Radio

1. Introduction

A recognized need within the Army is a cost effective, high performance solution to current and future battery needs to power an increasingly diverse array of portable electronic equipment. Rechargeable battery technologies have been recognized as a viable method of lowering per use battery costs, especially for non-wartime exercise, although for effective implementation higher performance rechargeable batteries are required to realistically simulate their primary counterparts. Further, in certain applications, high performance rechargeable batteries are more desirable than primary cells.

When cost is of little issue, primary Li/SO_2 batteries are often the technology of choice. The Li/SO_2 chemistry offers exceptional specific energy and energy density and is operational over a broad temperature range. For example, Li/SO_2 based BA-5590 batteries offer approximately 150 W h/kg and 175 W h/l (at the battery level) and are operational over the temperature range −40°C to 55°C. However, to alleviate the high cost of primary batteries, lower cost rechargeable batteries have been developed for non-wartime operation. In most cases, rechargeable substitutes utilize the Ni–Cd battery chemistry, although recently some NiMH and Li-ion batteries have become available. The NiMH and Li-ion chemistries typically offer performance superior to Ni–Cd, but at higher cost. Performance data for recent commercial rechargeable cells is reported in Table 1.

Some military rechargeable batteries utilize commercially available cells assembled to form a military battery. Because the battery requirements of military applications often differ significantly from commercial specifications, the most optimal cell chemistry and design for a military battery can differ significantly from commercially available cells. As a result, the cell chemistry is often capable of better performance than is realized when commercially available cells are used in a military battery.

Yardney Technical Products recently entered a research and development program directed at developing a low cost, high performance rechargeable battery technology specifically designed for military application. This effort has focused on applying the low cost spinel Li-ion chemistry to high power radio applications such as the BB-X590 application. By designing a space efficient prismatic cell and optimizing the chemistry for the intended application, performance comparable to that possible with the more expensive $LiCoO_2$ based Li-ion chemistry has been demonstrated using the lower cost spinel cathode materials.

Military high power radio battery requirements differ significantly from specifications typical for related consumer applications. For example, the BB-X590 battery specification requires initial capacity of 145 Wh and a maximum weight of 3 lb, or 106 Wh/kg and 164 Wh/l,

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Table 1
Performance data for recently available commercial cells

	Li-ion	NiMH	NiCd
Specific energy (Wh/kg)	266	282	120
Self discharge (%/month)	8	20	15
Energy efficiency (%)	96	55–65	55–75

and a 300 cycle life. While consumer applications typically call for much higher cycle life, up to 1000 cycles, specific energy and energy density requirements are not as demanding. Regarding temperature, the military specification calls for operation from −40°C to +70°C, with operation from −20°C to +55°C essential, whereas consumer specifications typically call for operation to +55°C and place less emphasis on operation below 0°C. In most applications, the rate capability and discharge profile of the cell is a high priority to ensure that the lower cutoff voltage for the device is reached after the cell has delivered a high percentage of its available capacity. This may be achieved by utilizing a cell chemistry which results in a flat discharge curve.

2. Approach

In this study, two cell designs were compared. The first was prismatic $LiMn_2O_4$/Graphite cells designed and fabricated at Yardney for a high power radio application. To minimize weight, a lightweight, rigid, plastic cell case has been utilized. Cells with this design have demonstrated specific energy of 110 Wh/kg and energy density of 194 Wh/l. The second cell design were cylindrical Sony $LiCoO_2$/C 18 650 cells of early 1996 vintage designed for commercial use. These cells utilize a steel cell case and likely a coke or hard carbon type anode material. Sony cells of this configuration have demonstrated over 110 Wh/kg and 266 Wh/l and exceptional cycle life, greater than 1000 cycles. The cells were of slightly different capacity (0.63 Ah for the $LiMn_2O_4$/C cell vs. 0.85 Ah for the $LiCoO_2$/C cell), thus the rates utilized in these experiments were normalized based on the cell capacity.

3. Performance

3.1. Discharge profile

Discharge profiles at a C/6 rate for a $LiMn_2O_4$ prismatic and a $LiCoO_2$ cylindrical cell are shown in Fig. 1. The shape of the discharge profile is determined by the cell chemistry, the flat 3.9 V discharge curve characteristic for a cell with a $LiMn_2O_4$ cathode and a graphite anode, the sloping discharge curve with average voltage 3.7 V characteristic for a cell with a $LiCoO_2$ cathode and a coke or hard carbon anode. The sloping discharge curve in the

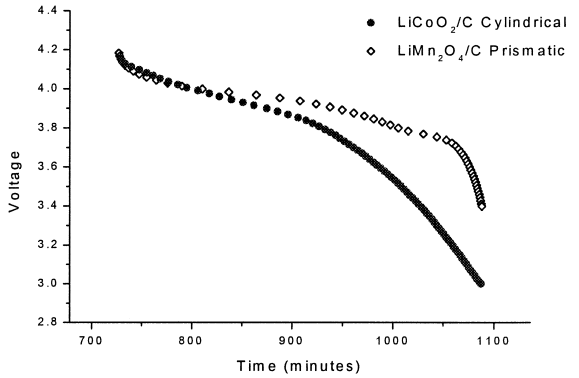

Fig. 1. Discharge curves for a Yardney prismatic design $LiMn_2O_4$/C cell and a Sony cylindrical 18650 $LiCoO_2$/C cell. The sloping discharge curve of the Sony cell is very useful for applications which require a state of charge indicator but results in reduced operational life for some applications.

Sony cell is very useful for applications which require a state of charge indicator as the cell voltage may be used to accurately indicate the state of charge, especially near the end of the operational life. For other applications, the sloping discharge curve may result in reduced operational life. If the $LiMn_2O_4$/C cells described in this example were used in a 6 cell BB-X590 application, which has a 20 V cutoff, 100% of the cell's available capacity could be utilized as at complete discharge (100% DOD) the cell voltage is 3.4 V. If a cell chemistry with a sloping discharge curve were used, 12% of the available capacity could not be utilized because when the cell voltage reaches 3.3 V (20 V for the battery), 12% of the cell's capacity would remain but could not be utilized as the battery voltage would be below the operational voltage of the device.

3.2. Rate capability

In a cell, the composition of the electrodes, the electrolyte, and the mechanical design of the cell greatly influence the rate capability. For example, designs which utilize high surface area electrodes, highly conductive electrolytes and minimize the cathode to anode distance, thereby minimizing cell internal resistance, are expected to offer better constant current and pulse rate capability. In this way, a low cost $LiMn_2O_4$ based cell designed for high rate discharge performance can offer exercise performance comparable to a more costly $LiCoO_2$ based cell designed for extended cycle life and moderate rate constant current discharge.

Considering the chemical diffusivity of lithium in the electrochemically active materials, one would expect $LiCoO_2$ to have better rate capability than $LiMn_2O_4$ as the diffusion coefficient of lithium in $LiCoO_2$ is regarded to be roughly 10 times greater than in $LiMn_2O_4$. For example, a number of authors [1,2] have determined the chemical diffusivity of lithium in $LiCoO_2$ to be near 10^{-8} cm^2

s^{-1} while others [3,4] have determined the chemical diffusivity of lithium in $LiMn_2O_4$ to be near 10^{-9} cm^2 s^{-1}. Others have determined different absolute values but they concur in that Li diffusion in $LiCoO_2$ is faster than in $LiMn_2O_4$. For example, Striebel et al. [5] recently determined the chemical diffusivity of Li in $LiCoO_2$ and $LiMn_2O_4$ thin films to be 10^{-10} cm^2 s^{-1} and 10^{-11} cm^2 s^{-1}, respectively. Chemical diffusion of Li in carbon anode materials [6] ($>10^{-8}$ cm^2 s^{-1}) is generally regarded to be faster than in $LiCoO_2$. Given the higher diffusivity of Li^+ in $LiCoO_2$ relative to $LiMn_2O_4$, in cells of equivalent design the cell incorporating the $LiCoO_2$ material would be expected to have equivalent or higher rate capability.

To compare the charge rate capability of the prismatic $LiMn_2O_4/C$ and the cylindrical $LiCoO_2/C$ cells they were charged at constant current rates ranging from C/10 to 2C and discharged at a C/5 rate to determine the capacity. The results of this experiment are shown in Fig. 2. In general the capacity of the cylindrical $LiCoO_2/C$ cell shows greater sensitivity to charge rate than the prismatic $LiMn_2O_4/C$ cell. This effect was small at rates below a C rate and greater above a C rate as emphasized by the steeper slope of the fitted curve in the case of the cylindrical $LiCoO_2/C$ cell. For example, after charging at a C rate, the cylindrical $LiCoO_2/C$ cell delivered 66% of the C/10 value but the prismatic $LiMn_2O_4/C$ cell delivered 77% of its C/10 value.

To compare the discharge rate capability of the $LiMn_2O_4/C$ and $LiCoO_2/C$ cells they were charged at a constant current C/5 rate and discharged at constant current rates ranging from C/10 to 4C. The results of this experiment are shown in Fig. 3. At low rates the discharge rate capability of the cylindrical $LiCoO_2/C$ cell and the prismatic $LiMn_2O_4/C$ cell are similar. For example, at a C rate the discharge capacity of the cylindrical $LiCoO_2/C$ cell was 88% of the C/10 value and the discharge capacity of the prismatic $LiMn_2O_4/C$ cell was 90% of the C/10 value. At higher rates the $LiCoO_2$ based cell demonstrated greater rate capability as might be expected considering the properties of the electrochemically active materials.

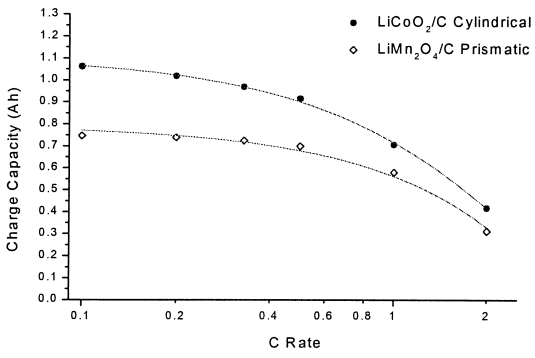

Fig. 2. Charge rate capability of a 0.85 A h $LiCoO_2$ /C Sony cylindrical cell and a 0.63 A h $LiMn_2O_4$ /C Yardney Prismatic Cell. The fitted curves are meant only as a guide to the eye.

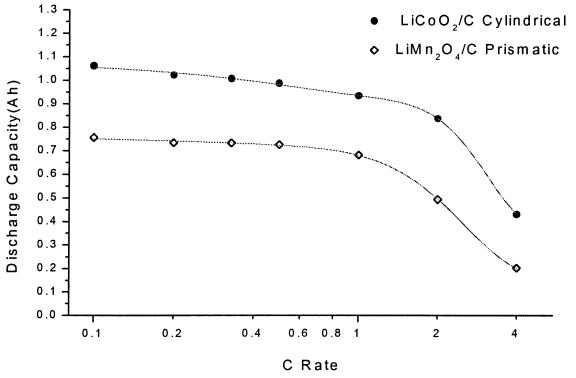

Fig. 3. Discharge rate capability of a 0.85 A h $LiCoO_2$ /C Sony cylindrical 18650 cell and a 0.63 A h $LiMn_2O_4$ /C Yardney Prismatic Cell. The fitted curves are meant only as a guide to the eye.

3.3. Pulse discharge—simulated radio operation

To compare the potential utility of these cells for high power radio use a simulated radio discharge test was conducted. The test consisted of a 1 min constant power simulated transmit at a $1.9E$ rate (E = Energy in W h) followed by a constant power simulated receive at a $0.38E$ rate. The test was begun with fully charged cells and continued until the cell voltage reached 3.0 V and 2.7 V for the $LiMn_2O_4/C$ and the $LiCoO_2/C$ cells, respectively. The cutoff voltages are typical for 100% DOD constant current cycling. During the test each cell's temperature was monitored by a thermocouple adhered to the cell case. The results of this test are shown in Fig. 4.

Both cells were able to service this discharge regime, the most noticeable difference being the operational life. The $LiMn_2O_4/C$ cell provided 130 min of service where as the $LiCoO_2/C$ cell provided 90.9 min of service for this discharge regime. The difference is largely due to the

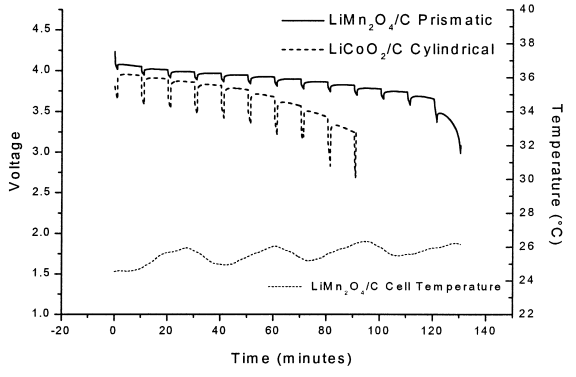

Fig. 4. Discharge curves for the $LiMn_2O_4$ /C and $LiCoO_2$ /C cells from the simulated radio test and below the temperature of the $LiMn_2O_4$ /C cell during the test, the temperature profile of the $LiCoO_2$ /C cell was identical.

shape of the discharge curve, the $LiMn_2O_4/C$ cell demonstrated a flatter voltage profile, expected considering the shape of the constant current discharge curves (Fig. 1) and the graphite anode material. The sloping discharge curve of the $LiCoO_2/C$ cell is characteristic for Li-ion cells with coke type anode materials. During the high power transmit pulses, the $LiMn_2O_4/C$ cell exhibited less voltage depression, typically 0.11 V vs. 0.38 V for the $LiCoO_2/C$ cell, likely related to the low internal resistance of the $LiMn_2O_4/C$ cell, measured by a DC pulse technique to be 43.4 mΩ. By the same DC pulse technique the $LiCoO_2/C$ cells averaged 97 mΩ internal resistance. The large voltage depression in the $LiCoO_2/C$ cell's discharge curve caused the cell voltage to reach the cutoff voltage prematurely, after the cell had delivered only 0.76 A h, or 89% of the rated capacity. In contrast, the capacity of the $LiMn_2O_4/C$ cell was completely utilized.

The temperature profiles emphasize the energy efficiency of the Li-ion chemistry, typically 96% under moderate rate constant current cycling regimes. The temperature profiles of both cells were identical and consisted of a slow undulation from the ± 0.3°C temperature instability of the test environment coupled with a 0.21°C rise in the cell temperature likely due to the high rate discharge process. For applications where thermal management is important, such as spacecraft or laptop computers, such high energy efficiency is advantageous.

3.4. Temperature dependence

Discharge curves at 50°C, 25°C and -10°C are shown in Fig. 6 for the $LiMn_2O_4/C$ cell. In this test the cells were charged and discharged at the specified temperature, a slightly more stringent condition than the current military test regime which calls for charging at 25°C and discharge at the temperature of interest. Relative to the 25°C data, the cell potential was 2.5 mV higher and 140 mV lower at 50°C and -10°C, respectively. At 50°C the discharge capacity was slightly above the 25°C value ($+1.8\%$) and at -10°C the discharge capacity was 18% less than the room temperature value.

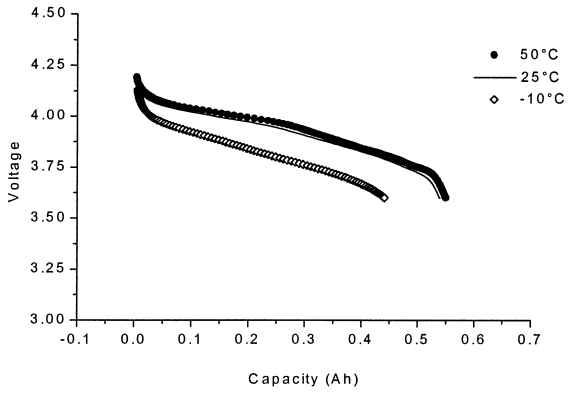

Fig. 5. Temperature dependence of the discharge profile at a C/5 discharge rate.

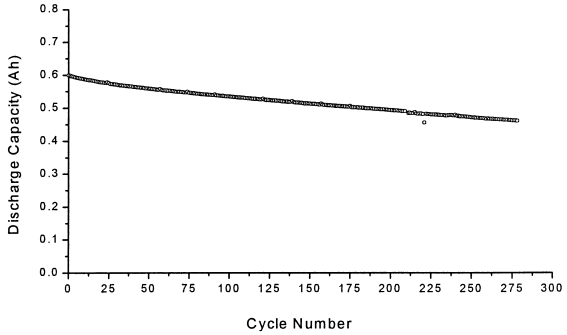

Fig. 6. Cycle life of a $LiMn_2O_4/C$ prismatic cell designed for high rate discharge operation. The cell was charged and discharged at a C/3.5 rate.

3.5. Cycle life

Li-ion batteries can be cost effective because of their long cycle life. Li-ion batteries which use $LiMn_2O_4$ also have the potential advantage of being less costly than $LiCoO_2$ based chemistries as $LiMn_2O_4$ is roughly 25% the cost of $LiCoO_2$. As reflected in recent Army battery specifications, battery calendar life is reached before the end of the functional life, thus cycle life beyond 300 cycles is rarely useful for current applications such as the BB-X590 or the BB-2847/U. Plotted in Fig. 5 is the discharge capacity of a $LiMn_2O_4/C$ prismatic cell vs. cycle number. In this high rate cell design pulse discharge capability has been achieved using low cost materials with some sacrifice to cycle life.

4. Conclusions

The potential utility of a low cost, high performance rechargeable Li-ion cell chemistry has been demonstrated and shown to offer performance comparable to a more costly Li-ion cell chemistry. The cell design demonstrated in this work was optimized for military high power radio battery application. By designing the cell for the intended use, the inexpensive $LiMn_2O_4/C$ cell chemistry and versatile prismatic design may be effectively applied to a wide array of applications. For cost-insensitive applications, materials such as $LiCoO_2$ or $LiNi_xCo_{(1-x)}O_2$ could be incorporated into this design to yield a higher capacity technology.

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