

## An update of the Li metal-free rechargeable battery based on $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ cathodes and carbon anodes

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### Abstract

We report on a rocking-chair cell using the manganese oxide spinel ( $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ ) as the positive electrode and carbon as the negative electrode, and detail its electrochemical behavior as a function of charge cutoff voltage, current rate, operating temperature, and the ratio of positive and negative electrode masses. Recently, the Li ion ( $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /electrolyte/carbon) laboratory test cells were optimized using a newly discovered liquid electrolyte system that (i) is compatible with the  $\text{LiMn}_2\text{O}_4$  positive electrode up to oxidation voltages of 5 V versus Li, and (ii) allows the use of petroleum-coke or graphite as the negative electrode. With this new electrolyte, the 3.7 V  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /carbon cells are readily reversible and show high specific energies (3 times more than Ni-Cd), high power rate capability, and promising cycle life even at 55 °C. 'AA' lithium metal-free rechargeable cells based on the  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /new electrolyte/carbon system were constructed for safety and performance evaluations. The unoptimized 'AA' cells are safe, have excellent rate capability and a capacity of approximately 0.35 A h.

### Introduction

Room temperature secondary lithium cells have been studied for the last two decades. Despite their promise (ability to deliver the highest specific energy among the rechargeable batteries) they are still not commercially-available because of safety problems associated with the use of pure Li metal and more specifically, the dendritic regrowth of Li upon cycling that might short-circuit the cell. A more advanced and inherently safe approach to Li batteries consists of replacing Li metal with a Li intercalation compound, leading to Li metal-free rechargeable batteries, the so-called 'rocking-chair' batteries [1-5]. This approach, proposed a decade ago, was realized with the recent announcement by two battery companies of the future commercialization of the 'rocking-chair' technology. The rocking-chair cells produced by Sony Energytec [6] and announced by Moli Energy [7] both use carbon as the negative electrode and  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  as the positive electrode, respectively.

Recently, we proposed another rocking-chair system [8-10] that uses the spinel  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  and selected this system over the system developed by Sony or under development by Moli for reasons that will be described later. In this paper we present the behavior of the  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /carbon cells and report on the behavior of a new liquid electrolyte composition that is resistant to oxidation up to 5 V and to reduction down to 0 V allowing good cycle life at room temperature and 55 °C for laboratory test cells and 'AA' cells based on the  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /carbon system.

## Experimental

All the results reported here were mainly obtained on laboratory Swagelock test cells that were assembled in a helium dry box. The composite positive and negative electrodes were made, as described earlier [9], by mixing respectively  $\text{LiMn}_2\text{O}_4$  and carbon (petroleum coke or graphite) with small amounts of binder and carbon black as electronic media. Prototype AA-type cells were made at Moli Energy (1990) using their hardware and design.

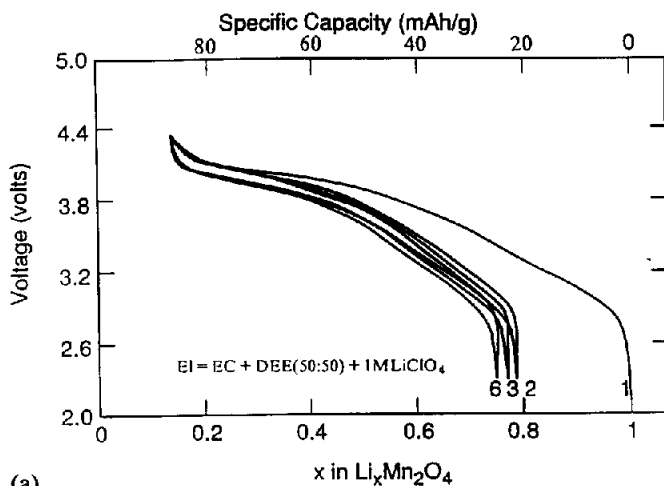
## Results

Previously [9, 11] we reported good reversibility for our positive electrode material  $\text{LiMn}_2\text{O}_4$  versus Li as well as for our negative electrode (petroleum-coke) versus Li using 1 M  $\text{LiClO}_4$  in ethylene carbonate–diethoxyethane (EC–DEE) (50:50) as the electrolyte. A 20% capacity loss between the first and second cycle was observed and the usable capacity of petroleum-coke did not exceed 0.5 Li ions per 6 carbons. In a rocking-chair cell the Li ions are shuttled back and forth between two Li ‘sponges’. To optimize such a cell, the capacity of the two Li sponges must be balanced (i.e., determine the relative masses of the positive and negative electrode required) so that when the cell is fully charged, the positive electrode is completely delithiated and the negative electrode fully lithiated. We found by means of a three-electrode cell that our system is optimized and operates safely when the mass ratio of positive to negative electrodes is 2.1 and when the charging voltage is limited to 4.4 V. The room temperature behavior of such a cell is shown in Fig. 1(a). The cell capacity is 100 m A h/g of positive electrode material. However, this capacity could be improved if one could find a way (i) to compensate for the large loss (20%) at the carbon negative electrode and/or to increase the capacity of carbon, and (ii) to enhance the actual capacity of  $\text{LiMn}_2\text{O}_4$  that is limited to 0.85 Li per formula unit.

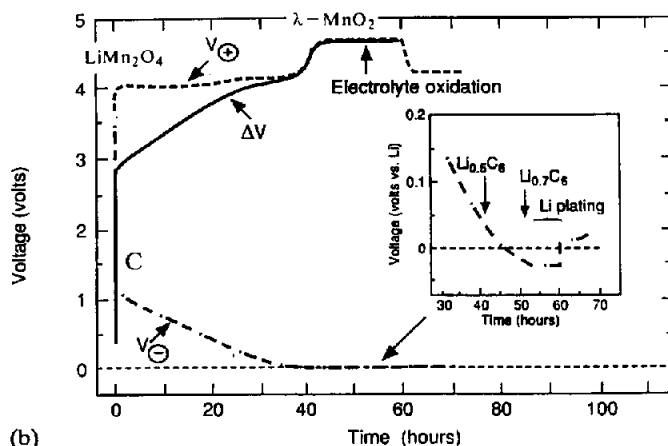
Figure 1(b) shows what happens when the charge voltage of the rocking-chair cell is poorly controlled (i.e., the cell is overcharged). The voltage of the battery stabilizes at a potential of 4.5 V upon charging, which corresponds to the decomposition of the  $\text{LiClO}_4$ -based electrolyte on the positive electrode. Simultaneously, the voltage of the negative electrode reaches zero, and the maximum capacity of the carbon electrode of 0.7 Li per 6 carbons is exceeded resulting in Li plating (see insert). The oxidation of the electrolyte often generates gaseous by-products that increase the internal pressure of the cell, thereby increasing the risk of rupture. Consequently, the room temperature charging voltage of these cells has to be maintained below 4.5 V for safe operating conditions. More importantly at 55 °C, because of the enhanced kinetics, the cutoff voltage needs to be lowered to 4.1 V so that the voltage of the positive electrode remains lower than 4.3 V versus Li, thereby limiting the capacity of the cell to 75% of its initial capacity. Thus, to take full advantage of this system one needs an electrolyte that is stable against oxidation up to a high voltage with minimum oxidation current to enhance the cycle life and improve the temperature performance of practical rocking-chair batteries. Next, we present our approaches to solving the above problems, that resulted in an enhancement for both capacity and safety of these cells.

### Enhancement of the capacity: lithium reservoir

Because of the irreversibility of the negative electrode during the first cycle, 20% of the Li is lost. A simple way to compensate for such a loss is to start with a positive



(a)



(b)

Fig. 1. The cycling behavior at room temperature of (a) an optimized  $\text{LiMn}_2\text{O}_4/\text{EC-DEE}(50:50) + 1 \text{ M LiClO}_4/\text{petroleum coke}$  rocking-chair cell at a rate of  $C/10$  with a ratio  $r$  of 2.1 (see text) and (b) the room temperature behavior of a three-electrode  $\text{LiMn}_2\text{O}_4/\text{EC-DEE}(50:50) + 1 \text{ M LiClO}_4/\text{petroleum coke}$  rocking-chair cell at room temperature when overcharged to a voltage higher than 4.55 V is depicted. The voltage of the carbon electrode vs. Li is shown in the insert.

electrode that contains Li in excess and is not moisture sensitive. The spinel phase  $\text{LiMn}_2\text{O}_4$  can reversibly intercalate a second Li at an average potential of 3 V versus Li leading to the  $\text{Li}_2\text{Mn}_2\text{O}_4$  phase. Past reports [12] indicated that the  $\text{Li}_2\text{Mn}_2\text{O}_4$  phase prepared from  $n\text{-BuLi}$ , is moisture sensitive. We, however, recently reported a novel way [8] to prepare moisture stable (at least for times as long as a few months)  $\text{Li}_2\text{Mn}_2\text{O}_4$  using a mild reducing agent such as  $\text{LiI}$  whose reduction potential is close to 3 V. This novel process has the advantage that at a fixed temperature and for a fixed amount of solvent (acetonitrile) and  $\text{LiMn}_2\text{O}_4$  powder, one can adjust the amount of  $\text{LiI}$  added to obtain  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  powders with any suitable  $x$  value. Using a three-electrode cell, we determined that the amount of excess Li needed in our starting

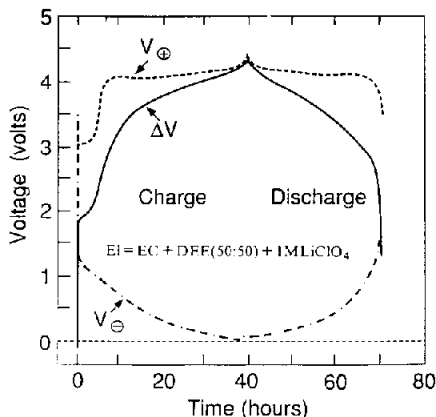


Fig. 2. Typical room temperature cycling behavior between 4.35 and 2.3 V of  $\text{Li}_{1.1}\text{Mn}_2\text{O}_4/\text{EC-DEE}(50:50) + 1 \text{ M LiClO}_4/\text{petroleum coke}$  cell, as measured in a three-electrode experiment, showing the advantage of the Li reservoir.

material to compensate for Li loss at the negative electrode is 0.1. Figure 2 shows the experimental result of a three-electrode cell and indicates that by using the second intercalation plateau of the spinel as a Li reservoir, the capacity of these cells can be enhanced by 10%.

Besides increasing the overall capacity, the use of  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  allows the discharge of rocking-chair cells to 0 V without jeopardizing the cycle life, while  $\text{LiMn}_2\text{O}_4/\text{carbon}$  rocking-chair cells rapidly lose capacity in the same conditions. Indeed, our three-electrode experiment with  $\text{LiMn}_2\text{O}_4$ , as the positive electrode has shown that carbon is fully delithiated while the spinel is not fully lithiated back (in the 3.9–4.0 V voltage range versus Li) when the rocking-chair battery is in the discharged state, leading to an increase of the carbon voltage up to 3.9 V versus Li when the rocking-chair is discharged to 0 V. At this high voltage the copper current collector oxidizes (Cu and Ni, usually used as current collectors for the negative electrode, oxidize above 3.5 V versus Li) leading to irreversible capacity, which compromises long life cycling behavior of the rocking-chair cell. In contrast, the use of  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  of appropriate composition allows for adjustments to the reversible capacities of both electrodes, leading to fully-intercalated  $\text{LiMn}_2\text{O}_4$  and fully-deintercalated carbon in the discharged state of the rocking-chair. Three-electrode experiments confirm that properly adjusted electrodes exhibit a voltage of 3.1 to 3.4 V when the rocking-chair is fully discharged, enabling the safe use of AA cells with copper current collectors.

### New electrolyte

In our search for new electrolytes we examined hundreds of compositions, since the catalytic activity of the desired positive electrode cannot be predicted. As a result, we discovered a group of  $\text{LiClO}_4$ -free electrolyte compositions whose effective range of stability extends to almost 5 V at room temperature as well as at 55 °C. (For confidentiality reasons the electrolyte composition cannot be given here; therefore the essential properties of this electrolyte are reported in Table 1.) Note the wide temperature stability range of this electrolyte as well as its acceptable ionic conductivity even at

TABLE 1  
Characteristics of the new electrolyte

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LiClO <sub>4</sub> free
Electroactivity range
0–5.0 V versus Li at room temperature
0–4.8 V versus Li at 55 °C
Temperature stability range
–20–130 °C
Ion conductivity
20.7 mS/cm at 65 °C
10.6 mS/cm at 25 °C
5.0 mS/cm at 0 °C
1.2 mS/cm at –20 °C
Compatible down to 0 V versus Li with petroleum-coke and graphite

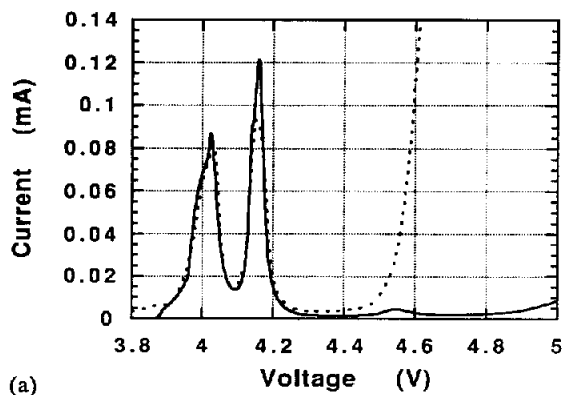
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–20 °C. More important is its ability to withstand oxidation under recharging voltages greater than 4.5 V as shown in Fig. 3(a) and (b), where we compared the stability of the earlier LiClO<sub>4</sub>-based electrolyte to the new one. For all plots, the first two current peaks observed with increasing the voltage correspond to the deintercalation of Li from the spinel LiMn<sub>2</sub>O<sub>4</sub>. With the old electrolyte we observed an exponential increase of the current at a voltage of 4.5 V indicating electrolyte oxidation. Because of the kinetics governing this process the electrolyte oxidation occurs at a lower voltage (4.3 instead of 4.5 V) at 55 °C (dashed curve in Fig. 3(b)). In contrast, with the new electrolyte (solid curve) no sharp features are observed in the *I* versus *V* curve above 4.3 V, either at room temperature or at 55 °C. The negligible current measured from 4.3 V up to about 5 V versus Li at both room temperature and 55 °C indicates remarkable stability of this new electrolyte system against oxidation.

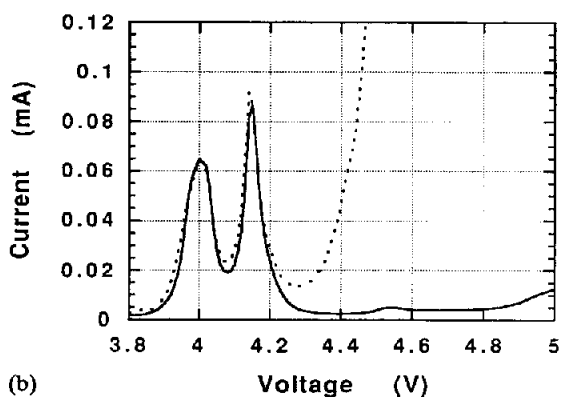
The voltammogram in the high voltage range is shown in Fig. 4. Note within this range the appearance of two weak peaks located at 4.5 and 5.0 V, respectively. These peaks are perfectly reversible on cycling and they correspond to the removal of 0.08 Li ions from the spinel (as confirmed by X-ray). Thus, the stability of this new electrolyte against oxidation allows complete delithiation of the spinel LiMn<sub>2</sub>O<sub>4</sub>, a result that was not achieved until now. The origin of these two peaks and their importance for minimizing electrolyte oxidation and optimizing the synthesis of LiMn<sub>2</sub>O<sub>4</sub> will be reported elsewhere [13].

As expected, minimizing electrolyte oxidation results in an enhancement of the cycle life at room temperature and 55 °C, as shown in Fig. 5, where the capacity is plotted as a function of the cycle number for Li<sub>1+x</sub>Mn<sub>2</sub>O<sub>4</sub>/new electrolyte/carbon cells operating at a rate of *C*/2 (i.e., full discharge in 2 h). It is remarkable to note that after 1000 cycles at room temperature the capacity of the cell is still 75% of its initial value, while at 55 °C the capacity of the cell reaches 75% of its initial value after 170 cycles (the maximum that we have tried so far).

Besides showing a remarkable stability against oxidation, our electrolyte is also stable with respect to reduction down to 0 V. This is not only true with a petroleum-coke negative electrode but also for graphite-based negative electrode. Figure 6 shows the room temperature voltage–composition curve for a graphite/new electrolyte/Li cell.



(a)



(b)

Fig. 3. Comparative plots of cell current against charging voltage at (a) room temperature and (b) 55 °C for two  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4/\text{Li}$  cells using (---) our prior  $\text{LiClO}_4$ -based electrolyte, and (—) our new  $\text{LiClO}_4$ -free electrolyte.

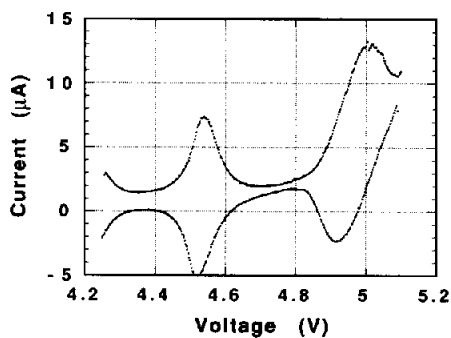
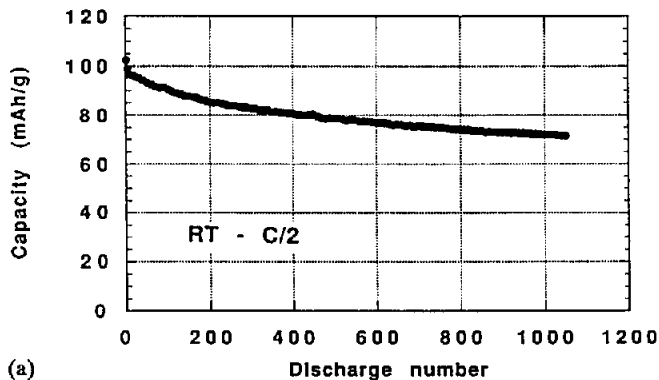
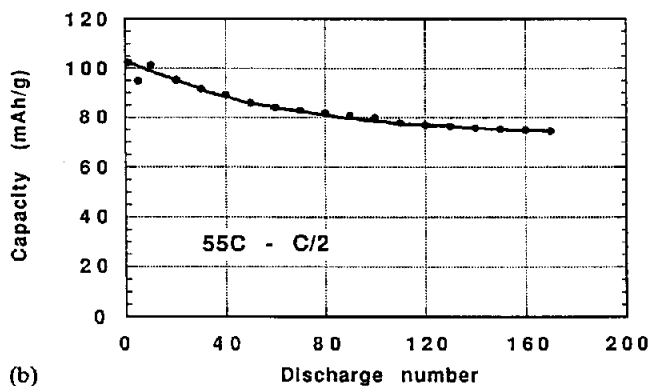


Fig. 4. Voltammogram in the high voltage range 4.3 and 5.1 V for a  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4/\text{Li}$  cell using the new electrolyte.



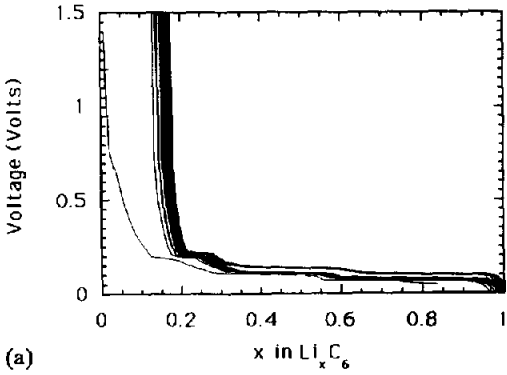
(a)



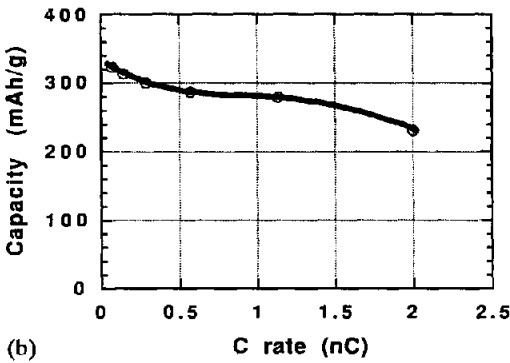
(b)

Fig. 5. Variation of the capacity as a function of the cycle number for two  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /new electrolyte/petroleum-coke laboratory-test cells operating (a) at room temperature, and (b) at 55 °C.

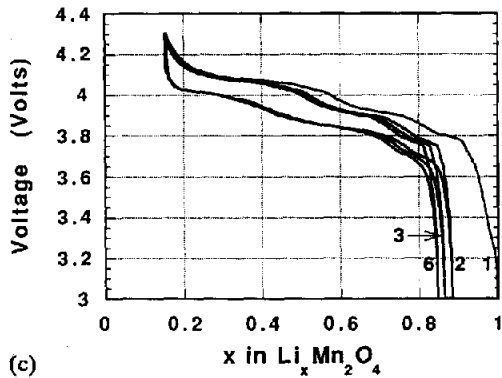
The cells were discharged from their rest voltage (3.4 V versus Li) to 0 V versus Li at a current rate of C/15 (full discharge in 15 h). The voltage trace curves show some anomalies corresponding to the well-documented staging phenomena that occur in graphite upon Li intercalation [14, 15]. The nonreversibility of such a cell during the first cycle is less than 15%. Afterwards, the cell shows excellent reversibility over  $\Delta x = 0.85$  in  $\text{Li}_x\text{C}_6$  corresponding to a capacity of 316 mA h/g of graphite material. At 55 °C, the behavior is similar to that observed at room temperature with excellent reversibility upon cycling. We studied carefully the effect of the current rate and particle size on the reversibility of the negative electrode for cells discharged down to 0 V. The main result is that for a same current rate, the reversibility of the Li intercalation process in graphite is strongly dependent on the graphite particle size with better rate performance and less irreversibility for very fine particles ( $< 1 \mu\text{m}$ ). Indeed, no change was observed in the capacity of a carbon/electrolyte/Li cell using very fine graphite particles discharged to 0 V when the current rate was increased from C/15 to C/2 (Fig. 6(a)). At higher rate a reduction in capacity was observed because of the limiting cutoff voltage as was confirmed by the recovery of the capacity when the discharge voltage was lowered to negative value (the reason for such a negative voltage has been explained elsewhere [9]). To ensure that absence of Li



(a)



(b)



(c)

Fig. 6. Typical cycling behavior at 25 °C of a graphite/new electrolyte/Li cell (a) charged and discharged at a rate of  $C/15$  is shown; (b) the capacity as a function of various discharging rates for the same cell, and (c) the voltage–composition curves are shown for a  $\text{LiMn}_2\text{O}_4$ /new electrolyte/graphite rocking-chair cell cycled at a rate of  $C/15$ .

plating during these high rate experiments, a second identical cell was separately discharged to lower voltages in order to determine the voltage plateau corresponding to Li plating. Figure 6(b) indicates that electrodes constituted of very fine graphite particles not only have a large capacity but can also handle high current rates. Three-



electrode rocking-chair cells were constructed using  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  as the positive and graphite as the negative electrodes, and the optimized ratio of the positive to negative electrode was determined to be 2.8 compared with 2.1 with petroleum-coke was used, thereby enhancing the cell capacity by about 25%. The voltage composition curves are shown in Fig. 6(c).

Using this new electrolyte composition, cylindrical 'AA'-size research prototype cells using Bellcore's  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /carbon system were recently constructed at the Moli Pilot plant in Burnaby, Canada, and evaluated for their safety and performance. The cells are a six-layered design consisting of two copper and two aluminum foils as the current collectors for the negative (petroleum-coke) and positive ( $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ ) electrodes, respectively. The two electrodes were electrically separated by two layers of a polypropylene separator (Celanese 2500). After winding the foils, they were inserted into nickel-plated steel 'AA' cans.

As yet there is no DOT (Department of Transportation) test for Li rechargeable battery safety, our 'AA' batteries were tested using three procedures: the 130 °C hot box test [16], the short-circuit test, and the JAWS test. The hot box test simply consists in placing a cell at 130 °C in a enclosure, monitoring the change in temperature of a cell through an external thermocouple, and recording the cell voltage as a function of time. A cell fails this test whenever there is a thermal runaway, fire or explosion. For the short-circuit test the positive and negative electrode are connected at time  $t_0$  and the current passing through the cell, the voltage of the cell, and the temperature of the cell, are measured continuously as a function of elapsed time. A cell fails this test when there is smoke, fire, or an explosion. Finally, the JAWS (i.e., spot welder) test, whose goal is to simulate the consequences of local heating of the cell (e.g., resulting from an internal short-circuit) consists of heating the cell at one spot to red, by means of a JAW operating at a constant power, and determining the length of time needed for a cell event to occur, either venting, smoke, fire or explosion. Our cells passed each test and in each case the safety vent functioned properly with the cell welds and casing remaining intact after the experiment.

Cycling studies were performed on 'AA'-size cells charged and discharged at a rate of 80 mA. Figure 7(a) shows a typical cell capacity as a function of the cycle

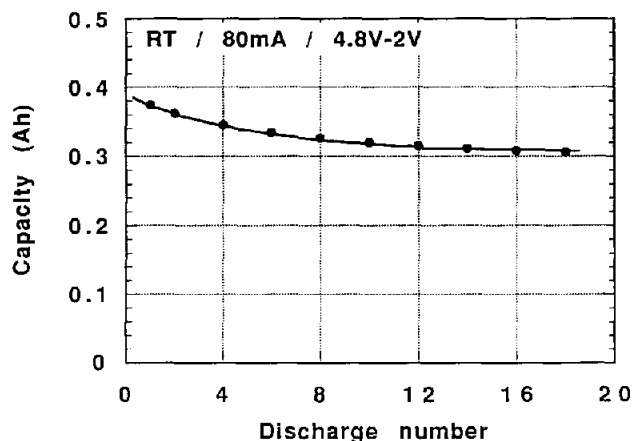


Fig. 7. The capacity of a nonoptimized  $\text{LiMn}_2\text{O}_4$ -based 'AA' cell is shown as a function of the cycle number.

number (20 cycles obtained to date). Note that the capacity, initially 380 mA h (Fig. 7(a)) decreases rapidly and then levels off at about 310 mA h after a few cycles. This behavior is similar to that seen in our laboratory test cells where a flat capacity-cycle number curve is obtained after about 20 cycles.

These are the first results obtained with 'AA' cells for the  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /carbon system, so improvements in capacity can be expected. For example, only single-coated copper or aluminum metals were used in these cells; the use of double-coated foils would increase the capacity. Also, as shown above, the replacement of petroleum-coke by graphite would increase the capacity of the cell by about 25% (assuming that the packing density of petroleum-coke and graphite are similar) so that a value of  $\approx 0.40$  A h for 'AA'-size cells could be expected. In Table 2, we compared the performance of  $\text{LiMn}_2\text{O}_4$ -based 'AA' cells with those of other rocking-chair systems and other competing aqueous systems such as Ni-Cd or Ni-metal hydride. The unoptimized  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ -based 'AA'-size cells show performances comparable with  $\text{LiCoO}_2$ -based 'AA' cells commercialized by Sony while their specific energy density is of about 1.5 and 3 times greater than for similar size Ni-metal hydride and Ni-Cd cells, respectively.

Finally, important parameters for some applications (namely microelectronics) are the rate capability of a battery and the amount of energy that can be delivered when discharged to 2.9 V, the lower voltage limit for microelectronic applications. This information was obtained by a multiple discharge of a cell down to 2.9 V at currents of 500, 250, 125 mA, ..., with a relaxation time of 15 min between each step. It is interesting to note, that within this voltage range, at least 90% of the capacity of an 'AA' cell can be utilized (Fig. 8). Similar measurements down to 2.5 V did not result in an noticeable enhancement of the capacity. The high rate capability for the Mn system could be advantageous not only for discharge but also for rapidly recharging a cell.

This preliminary evaluation of the  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /carbon system in 'AA' cells shows that cells using our new electrolyte composition are safe, stable up to 5 V, and that the electrochemical performance characteristics (long cycle life, high rate capability) previously obtained with laboratory-test cells, can be extrapolated to 'AA' cells. These

TABLE 2

Compared performances of different rechargeable systems

Cell	Capacity		Average voltage (V)	Energy	
	(A h/kg)	(A h/l)		(W h/kg)	(W h/l)
$\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ -carbon 'AA'-prototype	20.5	48	3.7	75	180
$\text{LiCoO}_2$ -carbon [6] 'AA'-size	22	53	3.6	78	192
Ni-Cd 'AA'-size	25	72	1.2	30	87
Ni-MH <sup>a</sup> 'AA'-size	40	119	1.26	51	150

<sup>a</sup>Referring to ref. 17.

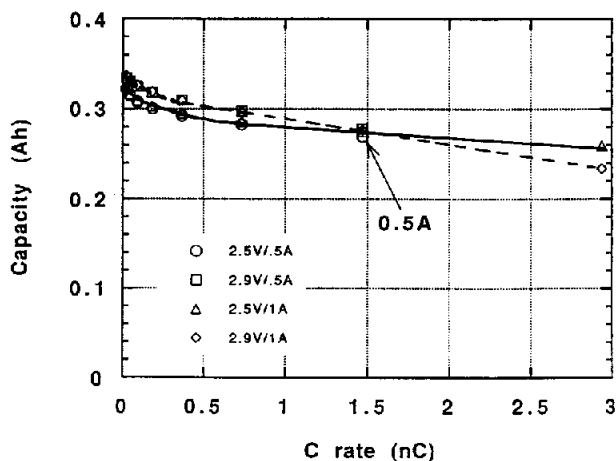


Fig. 8. The capacity of a nonoptimized  $\text{LiMn}_2\text{O}_4$ -based 'AA' cell is shown as a function of the ability of the cell to rapidly deliver their energy.

results confirm the promise we ascribed to this system and strengthen the position of the  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /carbon system as a serious candidate for the next generation of practical rocking-chair type batteries. In addition to the attractive safety aspects of this cell system,  $\text{MnO}_2$ , the precursor material in the synthesis of  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ , is at least 10 to 20 times cheaper than the cobalt or nickel oxides used for the preparation of  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$ , respectively. The cost of the electrode will become critical when the rocking-chair technology moves to cell sizes larger than 'AA'. Finally, an important advantage of manganese oxide-based materials is their extensive use in primary cells. Thus, concerns on toxicity, disposal, and recycling have already been addressed.

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