Electrochimica Acta, Vol. 38, No. 9, pp. 1221–1231, 1993
Printed in Great Britain.

0013–4686/93 $6.00 + 0.00
© 1993. Pergamon Press Ltd.

THE $Li_{1+x}Mn_2O_4$/C ROCKING-CHAIR SYSTEM: A REVIEW

J. M. TARASCON and D. GUYOMARD
Bellcore, Red Bank, NJ 07701, U.S.A.

(*Received* 15 *October* 1992)

Abstract—The new emerging rechargeable battery technology, called "rocking-chair" or "Li-ion", that uses an intercalation compound for both the positive and negative electrodes is safer than the battery technology using pure Li metal. In this paper we review our study of the Li-ion type battery based on the spinel $Li_{1+x}Mn_2O_4$ positive electrode and the negative carbon electrode. First we give a brief history of rocking-chair batteries, followed by a description of how to select and optimize intercalation materials for such a type of cell and then we present the main findings which allowed us to bring this battery system from concept to realization. Among the main findings are: (1) the use of the second Li intercalation plateau of the spinel as a Li reservoir; (2) the discovery of a new electrolyte composition resistant against oxidation up to 5 V; and (3) the ability to reversibly intercalate 0.9 Li ions into graphite at high rate with a small reversible loss. Based on these findings, AA research prototype cells with enhanced safety characteristics were constructed. We report on the performance of these cells, compare our results with existing or emerging battery technologies such as NiCd or Ni metal hydrides, respectively, and discuss problems inherent to the Li-ion technology.

Key words: intercalation, battery, Li-ion.

INTRODUCTION

For the last two decades an increasing interest in Li batteries (*eg* a battery that uses Li metal as the negative electrode) has developed amongst battery manufacturers. One reason for this is the high specific capacity (3800 Ah kg^{-1} of lithium compared to only 260 Ah kg^{-1} for lead). In addition, Li is also a highly electropositive metal, leading to high voltage cells. With this combination of properties, Li-based batteries are expected to have energy densities much larger than other systems.

To date, only primary lithium cells (among them CuO/Li, MnO_2/Li and FeS_2/Li systems) have been commercialized. In contrast, the development of secondary Li cells (*eg* cells that consist of an intercalation compound as the positive electrode) has been slow because of safety problems associated with the use of Li metal as the negative electrode[1–4] and due to problems stemming from dendritic regrowth of Li upon cycling that might short-circuit the cell.

A more advanced and inherently safe approach to rechargeable Li batteries, proposed a decade ago[5–9], is to replace Li metal with a material able to reversibly intercalate Li ions. This has been called the "rocking-chair" battery because Li ions rock back and forth between the intercalation compounds during charge/discharge cycles (Fig. 1). The output voltage of such a cell is determined by the difference between the electrochemical potential of Li within the two Li intercalating electrodes. It is important to have as the positive and negative electrodes, cheap compounds which can reversibly intercalate Li at high and low voltages, respectively. The Li intercalation voltage for some intercalation compounds is shown in Fig. 2. Among the materials proposed for replacement of Li metal are LiAl, WO_2, MoO_2[10], Mo_6Se_6[11] or carbon[12–14], with the latter providing the best compromise between large specific capacity and reversible cyling behavior. However, in rocking chair cells a price is paid in terms of average

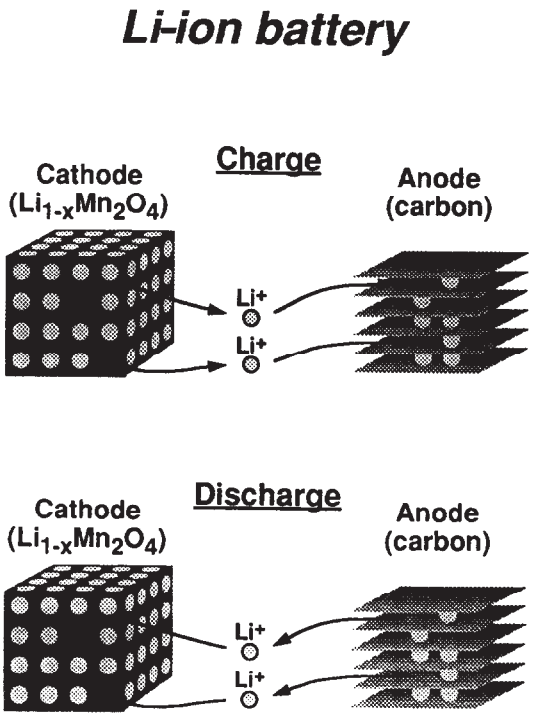


Fig. 1. The charge and discharge mechanism for a Li-ion battery is shown (both the cathode and anode materials are intercalation compounds).

APPLE 1024

output voltage and energy density when compared to a lithium metal cell; thus strongly oxidizing compounds (*ie* compounds which reversibly intercalate lithium above 4 V) must be used as the positive electrode. So far, as indicated in Fig. 2, there are only three Li-based compounds, $LiNiO_2$, $LiCoO_2$ and $LiMn_2O_4$ that satisfy this requirement. These Li-bearing positive electrode materials are not moisture sensitive and can be handled in ambient atmospheres as can Li free carbon negative electrode materials. The Li-ion cell is assembled in its discharged state, where the output voltage is close to zero. As with the Ni–Cd cells, they need to be charged prior to use.

Recently, Sony Energytec[15] announced the commercialization of a battery based on this concept. The Li-ion rechargeable battery developed by Sony used the layered $LiCoO_2$ intercalation compound as the positive electrode and a form of carbon (petroleum coke) as the negative intercalation electrode. Following up on this success, Moli Energy Ltd. (1990) is developing a battery using the same concept[16, 17], but using the layered compound $LiNiO_2$ as the positive electrode instead of $LiCoO_2$. Herein we will review Bellcore's work on rocking-chair type batteries using the $Li_{1+x}Mn_2O_4$ spinel phase as the positive electrode and a form of carbon as the negative electrode[18–20].

Our $LiMn_2O_4$/C rocking-chair system shows similar performances, to the Sony and Moli systems, with the exception that the specific capacity is about 5% smaller. However, the use of the spinel manganese oxide material offers the following advantages: (1) a lower overall electrode cost coming from an easier synthesis (only one low temperature step) and the use of Mn which is naturally more abundant and cheaper than Co or Ni; and (2) the low toxicity, a well known characteristics of the widely used manganese-based oxide materials. A large number of procedures have already been developed for the recovery of MnO_2 from alkaline–zinc batteries[21] and there has been extensive work on the recovery of lithium metal from minerals[22].

Another advantage of the $LiMn_2O_4$ system[23–26] over the $LiCoO_2$ and $LiNiO_2$ systems is that

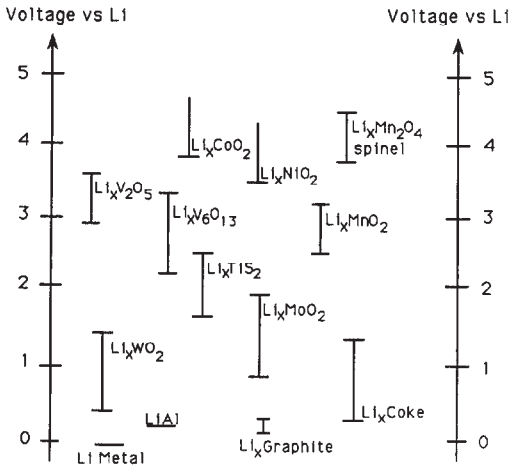


Fig. 2. Electrochemical potential range of Li intercalation (as measured with respect to Li metal) for a wide variety of compounds are shown.

$LiMn_2O_4$ can intercalate a second lithium atom at an average voltage of 3 V (*ie* a potential at which Li-based materials should be barely moisture sensitive if synthesized under mild conditions). We will show how this second plateau can be used as a lithium reservoir to improve the specific capacity of these batteries by 10% (a property unique to the spinel system) and detail a new way to synthesize $Li_{1+x}Mn_2O_4$ powders of well defined composition, x. An problem inherent to rocking-chair technology, is the risk of electrolyte oxidation at high operating voltages (>4 V). For instance, the voltage of the $Li_{1+x}Mn_2O_4$/Li couple is about 4.1 V and one would need to be able to charge the cell up to 4.5 V to take full advantage of this redox system. This means that the electrolyte of choice for this rocking-chair system must be stable over a voltage window ranging from about 0 to 5 V. We have found a new electrolyte composition with such a range of stability.

In this paper, we will illustrate and comment on the different problems faced in going from the idea of using the spinel $LiMn_2O_4$ as the positive electrode to the realization of rocking-chair prototypes based on this compound.

EXPERIMENTAL

The $LiMn_2O_4$ powders were prepared by reacting a mixture of Li_2CO_3 and MnO_2 powders in air, in an alumina crucible for three days, followed by two successive grinding and annealing sequences. An alternative route is the synthesis of $LiMn_2O_4$ at lower temperatures (<600°C) via a sol gel route that consists in using LiOH and Mn acetates as precursors[27] leading to small particle sizes (<2 μm). We have initially used petroleum coke and then graphite as intercalation materials for our negative electrode. A one molar solution of $LiClO_4$ salt dissolved in a 50/50 weight ratio of ethylene carbonate (EC) and diethoxyethane (DEE) was initially used as electrolyte.

The above intercalation compounds are mixed with binders and highly conducting powders prior to use in electrochemical test cells. The composite electrodes are made by dissolving a small amount of binder, either ehtylene propylene diene monomer (EPDM) in a solution of cyclohexane, or polyvinylidene fluoride (PVDF) in a solution of cylopentanone, and by adding the appropriate amounts of intercalation compound and black carbon to this solution. The resulting slurry is deposited onto an aluminum disk for the positive electrode, and onto a copper disk for the negative electrode and then dried at 150°C for 1–2 h.

All the electrochemical measurements were carried out using Swagelock laboratory test cells. Depending upon the type of measurements performed, two or three electrode cells were used. A "Mac Pile" system[28] that can operate ether in a galvanostatic or potentiostatic mode was used to perform the measurements. In the galvanostatic mode, the output voltage of the cell was monitored while the cell delivered a constant current. From the elapsed time and the amount of current one can deduce the

amount of intercalated species x in $Li_xMn_2O_4$ or the capacity of the cell (a more meaningful number for battery manufacturers). In the potentiostatic mode, the current was monitored while the voltage was scanned at very low rate (10–50 mV h^{-1}).

RESULTS

The first step in the process of assembling a Li-ion cell consists in optimizing the electrochemical behavior (cycling performance and rate capability) of each composite intercalation electrode with respect to lithium over a wide temperature range. A survey of several (s, t, u) mixtures, where s, t and u represent, respectively, the weights in % of intercalation compound, binder and black carbon was carried out. We found that a percentage weight ratio of [89:10:1] and [94:5:1] gives the best result for the positive and negative electrodes when EPDM is used and [90:5:5] and [80:5:5] when PVDF is used.

Figure 3a illustrates the cycling behavior of $LiMn_2O_4/LiClO_4$ based electrolyte/Li cells both at room temperature and at 55°C. At room temperature the cell was cycled between 3.4 and 4.5 V, but at 55°C the charge cut-off voltage was limited to 4.25 V because of risks of electrolyte oxidation. The spinel phase $LiMn_2O_4$ can rapidly and reversibly intercalate 0.8 Li per formula unit both at room temperature and at 55°C. However, note that only 0.9 Li per formula unit can be removed from $LiMn_2O_4$ during the first charge, while the nominal composition is 1.

The cycling behavior of a petroleum coke/$LiClO_4$ based electrolyte/Li cell using an optimized composite electrode is shown in Fig. 3b. After a subsequent loss of reversibility during the first cycle (25%), the carbon electrodes were found to rapidly and reversibly intercalate 0.5 and 0.55 Li per six carbons ($Li_{0.55}C_6$) (at room temperature and at 55°C, respectively). The range of reversibility of our petroleum coke electrode was increased to $x = 0.7$ when the discharge cut-off voltage was decreased to 2 mV vs. Li, but this voltage is undesirable for safety reasons, because it is too close to those required for Li plating. Thus, we have fixed 0.02 V vs. Li as the lowest voltage limit that our negative electrode can reach in order to rule out any risk of Li plating.

The delithiation of the spinel occurring during the charge of a $LiMn_2O_4$/Electrolyte/Li electrochemical cell to 4.3 V vs. Li results in a λ-MnO_2 phase. This phase was reported to be metastable and to decompose upon heating in air into a non Li-intercalable β-MnO_2 phase[29]. Temperatures ranging from 60 to 300°C have been reported for this conversion. The conversion of the spinel could limit the usefulness of the $LiMn_2O_4$ phase in a practical battery if it occurs at low temperature, so we investigated this phase decomposition by means of both differential scanning calorimetry (DSC) and X-ray diffraction measurements. We found, as shown in Fig. 4, that this phase transformation occurs at 180°C, but can also be obtained at lower temperatures if lower heating rates are used. In contrast to previous reports, we did not observe a direct phase conversion to β-MnO_2, but rather an evolution of the λ-phase to the ε and then finally to the β-MnO_2 phase. Finally, powders left at 55°C for three months were still pure λ-MnO_2, as determined by X-ray analysis, ensuring that rocking-chair cells based on this material could operate to 55°C without risk of failure due to an electrode phase conversion.

In a rocking-chair cell the amount of positive and negative electrode materials has to be adjusted in a

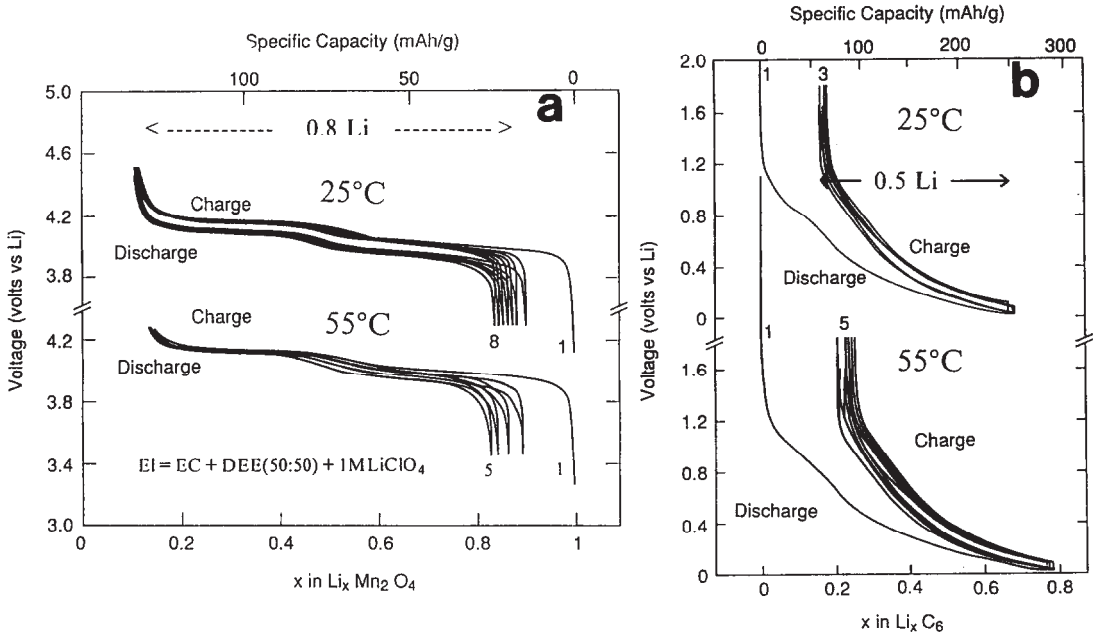


Fig. 3. The typical cycling behavior at 25 and 55°C for a $LiMn_2O_4$/EC + DEE(50:50) + 1 M $LiClO_4$/Li (a) and a C (petroleum coke)/EC + DEE(50:50) + 1 M $LiClO_4$/Li (b) is shown. The spinel-based cell was cycled at a C/10 rate in contrast to C/20 for the carbon-based cell. EC = ethylene carbonate, DEE = diethoxyethane.

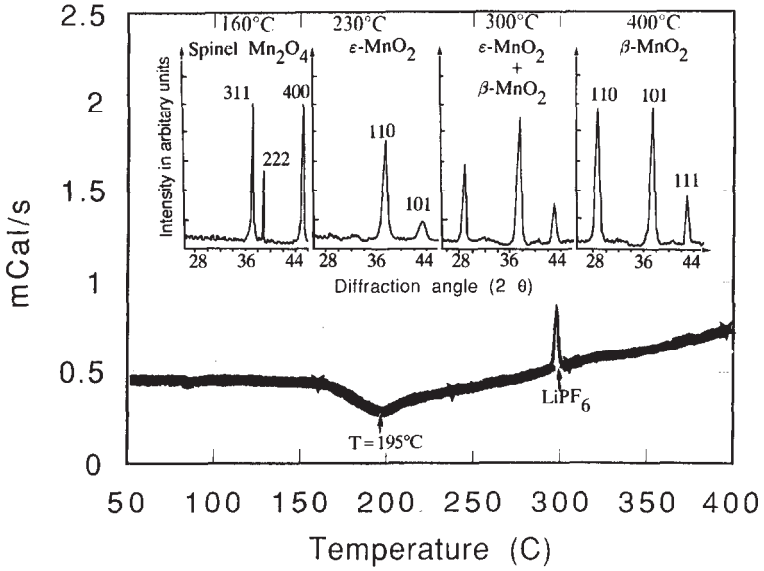


Fig. 4. Differential scanning calorimetric measurements (DSC) for a delithiated $LiMn_2O_4$ (*ie* λ-MnO_2) sample (see text). The phase transformation occurs at 195°C. The inset shows the X-rays taken at position marked by asterisks on the DSC curve. The ambient was air and the temperature rate of 2°C per min.

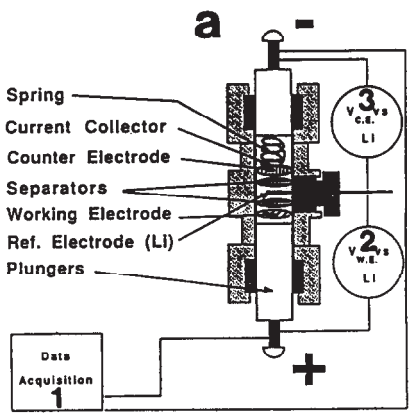
way that the reversible capacity of each electrode is equalized for both safety and optimum performance. In short, with this technology it is necessary to balance the weight of the two electrodes so that when $LiMn_2O_4$ is fully charged (*ie* delithiated) the negative intercalation electrode has to be fully lithiated with its voltage close to 0.02 V vs. Li. To determine accurately such a ratio, we have used a three electrode Swagelock cell (Fig. 5a) where we simultaneously monitor the voltage of each electrode vs. a Li reference electrode as well as the output voltage of the cell. From these measurements we deduced that the optimum ratio is 2.1 (Fig. 5b). For such a ratio, the $LiMn_2O_4$ spinel phase is fully delithiated when the voltage of the negative electrode vs. Li reaches 0.02 V. The effect of changing the ratio r on both the safety and performance behavior of a rocking-chair cell is illustrated in Fig. 6. Ratios greater than 2.1 may result in Li plating that could jeopardize the cell safety. Ratios smaller than 2.1 result in poor use of the rocking-chair system and decreases its safety, since the potential can reach values above that of electrolyte decomposition of the electrolyte. This situation is illustrated in Fig. 7 where the cycling behavior of a rocking-chair with a ratio of 1.7 is shown. The overcharge cut-off voltage is limited to 4.5 V (4.6 V being the electrolyte decomposition potential at room temperature). However, note that on charge the voltage of the cell stabilizes at 4.5 V because of the electrolyte oxidation, by the positive electrode. (The potential at the positive electrode is 4.8 V vs. Li.) On subsequent cycles, even if the cell is kept lower than 4.4 V vs. Li, the voltage composition curve shows lower capacity and larger polarization than a cell that has not been overcharged. Most likely, the electrolyte decomposition results in the formation of film at the positive electrode that increases the internal cell resistance. This trend is enhanced by further cycling until the cell has no more capacity. These results indicate that for rocking-chair cells using $LiClO_4$ based electrolytes, once the oxidation of the electrolyte has been initiated, it cannot be stopped even by lowering the overcharge cut-off voltage on subsequent cycles.

An optimized cell with a ratio of positive to negative electrode of 2.1 was assembled and its first cycles are shown in Fig. 8. The cell is cycled at a rate of C/5 between 2 and 4.35 V. After the first cycle, the difference in voltage between charge and discharge is small indicating a good rate capability. The cell capacity decreases rapidly from the first to the second cycle and then levels off after the fifth and sixth cycle. This cell can reversibly intercalate 0.32 Li atoms per Mn atom at an average output voltage of 3.7 V, yielding an effective energy of 250 $Wh\,kg^{-1}$ (both positive and negative masses included). This is 2.5 times greater than that obtained with the well known Ni–Cd batteries.

The above results indicated that rocking-chair cells can indeed be made with $LiMn_2O_4$ as the positive electrode. However, before such a system can be used in a commercial product several problems need to be solved in order to enhance safety and improve performance.

The use of a $LiClO_4$ based electrolyte is not a viable option with respect to safety because of the explosive nature of the $LiClO_4$ salt. In addition, the narrow voltage window between the end of the lithium deintercalation in the spinel and the beginning of the electrolyte oxidation, 0.2 V at room temperature and 0 V at 55°C, limits the capacity of our system at 55°C, and does not provide a safety margin large enough in case of overcharge.

When a $LiMn_2O_4/LiClO_4$ based electrolyte/C cell is discharged to 0 V, the voltage of the negative electrode is equal to that of the positive electrode nearly 4 V vs. Li (a $LiMn_2O_4$/Electrolyte/Li has an open circuit voltage of 3.5 V). A reaction may occur



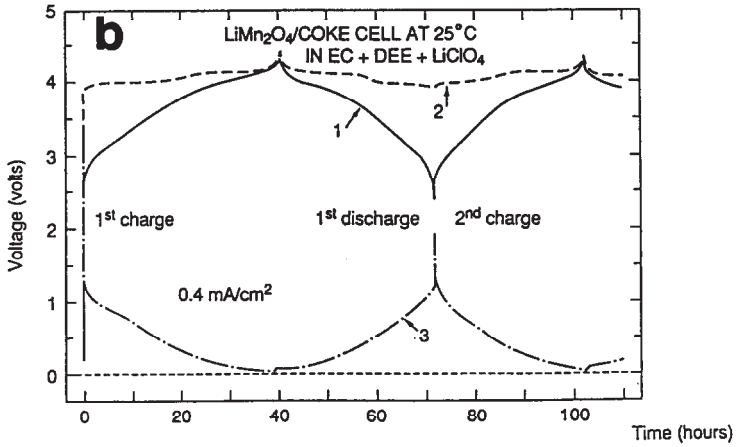


Fig. 5. The schematic of a three-electrode cell is shown in (a) and the first cycles at room temperature of a $LiMn_2O_4$/EC + DEE(50:50) + 1 M $LiClO_4$/C (petroleum coke) three-electrode cell, under constant current, are shown in (b). The voltage measured at the positions denoted 1, 2 and 3 on the cell schematic is plotted as a function of time in the bottom plot, curves 1, 2 and 3, respectively.

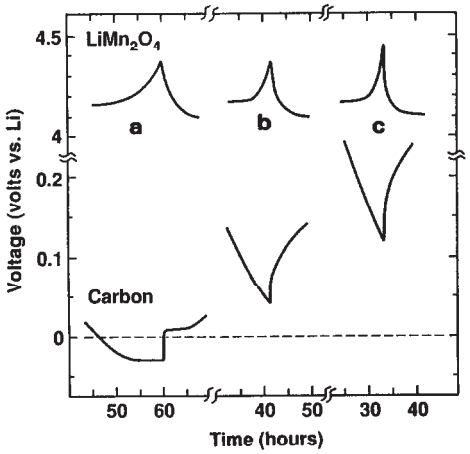


Fig. 6. Voltage profiles vs. Li (as measured from a three electrode cell) of $LiMn_2O_4$ and carbon electrodes at the end of the first charge and the beginning of the first discharge with different ratios $r = 3.1$ (a), $r = 2.1$ (b) and $r = 1.7$ (c). For these experiments the mass of the carbon electrode was maintained constant (30 mg), the electrolyte used was EC + DEE (50:50) + 1 M $LiClO_4$ and the current rate was 0.4 mA cm^{-2}.

between the copper current collector and the C electrode at voltages greater than 3.4 V vs. Li. Thus, a requirement for this rocking-chair system is the provision of an overdischarge protection allowing the cell to operate safely.

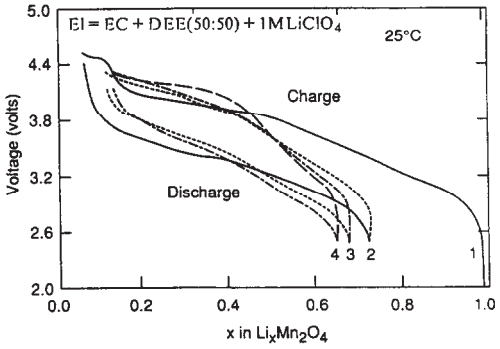


Fig. 7. The cycling behavior of a cell using a weight ratio (positive to negative electrode) of 1.7 (51/30 mg) is shown. The cell was cycled at 0.5 mA cm^{-2} between 0 and 4.5 V during the first charge and then between 2.5 and 4.35 on subsequent cycles.

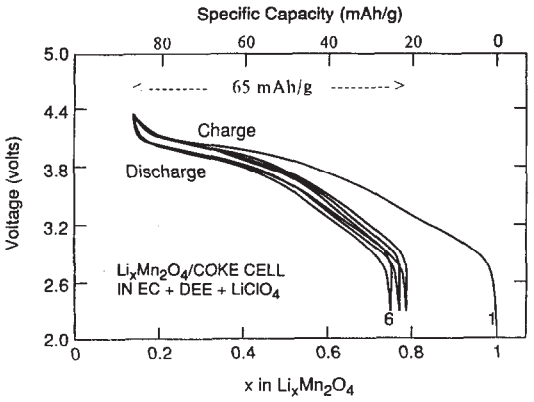


Fig. 8. Cycling behavior at room temperature of a $LiMn_2O_4$/EC + DEE(50:50) + 1 M $LiClO_4$/C rocking-chair cell at a rate of C/10 with the mass of the positive electrode being 2.1 times that of the negative electrode.

Finally, although the petroleum coke negative electrode gives the best compromise between capacity and cycling performance over other graphitic carbons it would be of tremendous benefit to improve the capacity of this negative electrode (*ie* using graphite instead of petroleum coke). The Li intercalation into graphite has been intensively studied for more than twenty years. Even the best results obtained so far show irreversible losses during the first cycle of 50% and poor rate capabilities, never exceeding C/30[15, 16]. Such a large irreversibility during the first cycle is not critical for cells having a Li negative electrode, however, in a rocking-chair type configuration where the amount of lithium is well defined by the amount of positive electrode, such a large loss is detrimental to performance. There is also a need to enhance the kinetics of the lithium intercalation process with graphite. In the next section we present our solutions to the above problems.

Li *reservoir within the spinel* $LiMn_2O_4$

We have previously shown that our petroleum coke electrode exhibits a 25% loss in reversibility during the first cycle similar to all the rocking-chair systems using a carbon negative electrode. This implies that a large amount of Li from the positive electrode is lost during the first recharge of the rocking-chair cell. Our $LiMn_2O_4$/petroleum coke rocking-chair system has been optimized with a mass ratio of 2.1 which takes into account the 25% capacity loss at the carbon electrode during the first cycle. However, in these cells, an excess amount of positive electrode [$(1 + x)LiMn_2O_4$] material is used to provide the extra amount of Li that is lost on the carbon negative electrode during the first cycle. This excess reduces the gravimetric and volumetric capacities of these cells. A way to overcome this problem would be to use the spinel structure with extra Li ($Li_{1+x}Mn_2O_4$) in such a way that the excess Li could be totally used to compensate for the 25% loss at the negative electrode. The construction of $Li_{1+x}Mn_2O_4$/C instead of $(1 + x)LiMn_2O_4$/C would result in a lower mass ratio (<2.1), leading to enhanced gravimetric and volumetric capacities for the Li–Mn–O based rocking-chair system. The spinel $LiMn_2O_4$ possesses a second reversible lithium intercalation plateau[23, 24] located at 3 V and we propose to use this second lithium intercation plateau as a lithium reservoir[18]. Indeed, by increasing the amount of Li in $Li_{1+x}Mn_2O_4$, the value of x may be adjusted to compensate for the loss of Li associated with the negative electrode, barely affecting the weight of the positive electrode. To take advantage of this unique property of the spinel, it is necessary to prepare air-stable $Li_{1+x}Mn_2O_4$ powders so that the manufacturing cost will remain unchanged. The synthesis of $Li_2Mn_2O_4$ has been reported[30] using *n*-BuLi as a reducing reagent and it was claimed that the reacting material was moisture sensitive. We identified the use of a strong reducing reagent such as *n*-BuLi as the source of the problem. We have tried a mild reducing reagent, such as LiI, and demonstrated the possibility of preparing air-stable $Li_2Mn_2O_4$ powders. Our chemical reaction simply involves refluxing $LiMn_2O_4$ powders in an acetonitrile solution of LiI for several hours.

The key advantage of this chemical reaction is that it allows preparation of $Li_{1+x}Mn_2O_4$ powders of well defined composition x as described in detail elsewhere. By fixing the amount of $LiMn_2O_4$ powder and the volume of acetonitrile and by using the Nernst equation, the redox potential of the solution at any state of the reaction x, and the amount of LiI needed to form a $Li_{1+x}Mn_2O_4$ powder of defined x may be calculated. Figure 9 illustrates this. Note that the reduction reaction can only occur when the redox potential of the solution is lower than the one of the $LiMn_2O_4/Li_2Mn_2O_4$ plateau. Finally, it should be possible to scale this process up.

Using the three electrode cell, we determined that the right amount of excess lithium in $Li_{1+x}Mn_2O_4$ to compensate for the loss associated with the negative electrode during the first cycle is $x = 0.1$. The behavior of a rocking-chair cell using $Li_{1.1}Mn_2O_4$

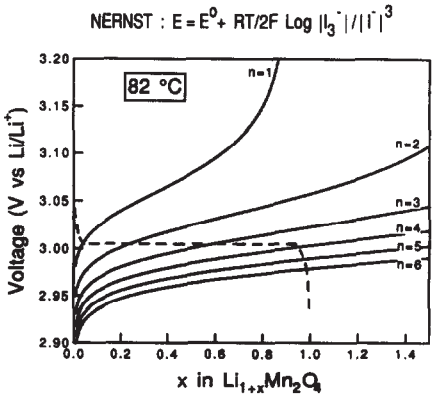


Fig. 9. A calculation of the Nernst equation at 82°C for the reaction: $LiMn_2O_4 + 3x/2\ LiI \rightarrow Li_{1+x}Mn_2O_4 + x/2\ LiI_3$ has been done in order to determine the amount of LiI needed to prepare $Li_{1+x}Mn_2O_4$ powders of any wanted lithium excess (x). The amount of $LiMn_2O_4$ has been fixed at 4 g, while nx4 g of LiI is used in 100 cm^3 of acetonitrile. The dashed curve represents the voltage of the $LiMn_2O_4/Li_2Mn_2O_4$ phase transformation measured at 82°C.

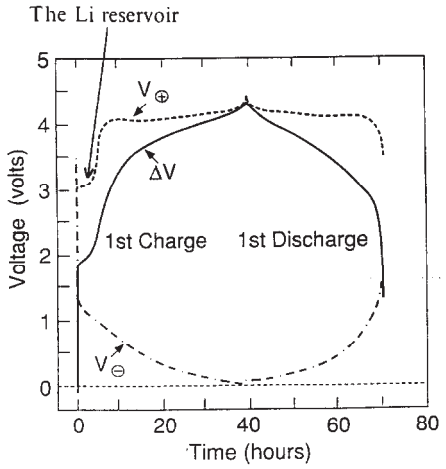


Fig. 10. The first cycles at room temperature of a $Li_{1.1}Mn_2O_4$/EC + DEE(50:50) + 1 M $LiClO_4$/C (petroleum coke) cell cycled between 4.35 and 2.3 V, as measured with the three-electrode configuration. The solid curve represents the output voltage of the cell, while the dashed and the dot-dashed curves represent, respectively, the voltage vs. Li of the $LiMn_2O_4$ and the carbon electrode.

powder as the positive electrode is shown in Fig. 10. We observed the removal of 0.1 Li at 3 V during the first cycle, and subsequent cycles without any further loss in capacity. The use of the Li reservoir results in an increase in the cell capacity by 10%. In addition, this extra lithium will limit the voltage of the negative electrode to 3 V (vs. Li) when discharging the rocking-chair cell to 0 V, and thereby acts as a safety switch for these cells in case of overdischarge.

New electolyte composition

We showed that 1 M $LiClO_4$ in a 50:50 mixture of ethylene carbonate (EC) and diethoxyethane (DEE) electrolytes begins to undergo oxidation at 4.5 V, and 4.3 V at 55°C. The electrolyte oxidation was found to result in solid and gaseous products, with the solid products forming a film that increases the polarization of the cell and decreases its output voltage, while the gaseous products increase the risk of explosion. Thus, to increase the cycle life of these batteries and to improve their temperature performance it is necessary to minimize the electrolyte oxidation. This search is purely empirical since the catalytic activity of the positive electrode material against electrolyte oxidation cannot be predicted. Numerous electrolyte compositions containing various ratios of salts, solvents and cosolvents were investigated for their ionic conductivity and resistance to oxidation. From this study a new $LiClO_4$-free electrolyte composition, resistant against oxidation to 5 V, compatible with carbon (both petroleum coke and graphite) and with high ionic conductivity over a wide temperature range was discovered. The oxidation current for this proprietary new electrolyte under highly oxidizing conditions (up to voltages of 5 V) is compared (in Fig. 11) to the oxidation current of our previous electrolyte under similar test conditions. In both plots, the peaks located at 4.0 and 4.15 V correspond to the removal of Li while the large increase of the current at 4.5 V at room temperature (Fig. 11a) and at 4.3 V at 55°C (Fig. 11b) for our $LiClO_4$-based electrolyte corresponds to its oxidative decomposition. In contrast, this rapid increase of the current upon increasing voltage is not observed for our new electrolyte above 4.3 V. Strikingly, the oxidizing current at 5 V remains very small even at 55°C, indicating an increased stability of this electrolyte against oxidation. However, several weak features can be observed on the *I* vs. *V* curve at voltages greater than 4.3 V. These anomalies become more pronounced in Fig. 11c where this part of the curve has been enlarged. This new set of reversible oxidation–reduction peaks, observed for the first time, corresponds to the removal of 0.06 lithium ion from the spinel.

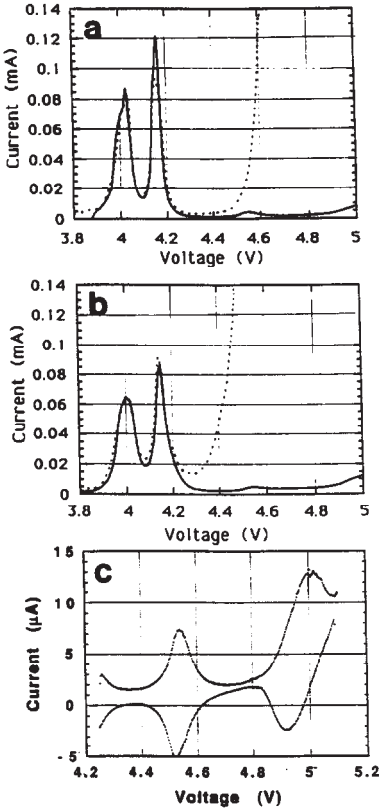


Fig. 11. Comparative plots of cell current against charging voltage at both room temperature (a) and 55°C (b) for two $Li_{1+x}Mn_2O_4$/Li cells using our prior $LiClO_4$ based electrolyte (dashed curve) and our new $LiCO_4$ free electrolyte (solid curve). The voltammogram in the high voltage range 4.3 and 5.1 V for a $Li_{1+x}Mn_2O_4$/Li cell using the new electrolyte is shown in (c).

This result shows why it is difficult to remove more than 0.9 Li from the spinel. The two capacity peaks are related to local structural defects (*ie* different environments for the Li ions) and their amplitude is extremely sensitive to the conditions of synthesis of $LiMn_2O_4$. The electrochemical performance of $LiMn_2O_4$ was found to be closely tied to the relative amplitude of these two peaks. In short, they can simply be used as fingerprints for preparing $LiMn_2O_4$ powders which will give the best electrochemical performance when used as positive electrode in a rocking-chair cell. A complete study

dwelling on the importance of these two peaks with respect to the optimization of the $Li_{1+x}Mn_2O_4$/Electrolyte/C system will be described elsewhere[31].

Besides allowing a better understanding of the importance of the synthesis conditions on the electrochemical behavior of $Li_{1+x}Mn_2O_4$ with respect to lithium, this newly discovered electrolyte has also increased the cycle-life of these rocking-chair batteries. Figure 12 shows the capacity plotted as a function of the cycle-number both at room temperature and at 55°C. It is remarkable to note that the cell capacity of a $Li_{1+x}Mn_2O_4$/Electrolyte/C cell, charged and discharged at a rate of C/2 between 2 and 4.7 V, is still higher than 60% of the initial capacity after 2300 cycles. Even at 55°C, when cycled under similar conditions, the loss in cell capacity is less than 20% of the initial capacity measured after the fifth cycle.

Carbon vs. graphite

The effective use of graphite as an intercalation material in a Li battery has been prevented by the inability of finding an electrolyte that: (1) minimizes the large irreversibility of the Li intercation process into graphite during the first cycle; and (2) allows for a fast intercalation rate. The best results so far were reported by J. Dahn *et al.*[32] (Fig. 13a) which shows successful intercalation of two lithiums per six carbons ("Li_2C_6") during the first cycle and one reversibly on subsequent cycles at a rate of C/40. He suggested that the formation of a superficial passivation layer on carbon (resulting from electrolyte reduction) controls the kinetics of the Li intercalation process into carbon, limiting the rate capability of the C/Electrolyte/Li cell. In spite of the low rate capability, the 50% loss during the first cycle is not tolerable with the present rocking-chair technology, because the amount of available lithium is defined by the amount of Li in the positive electrode. Thus, electrolytes that are compatible with graphite are needed.

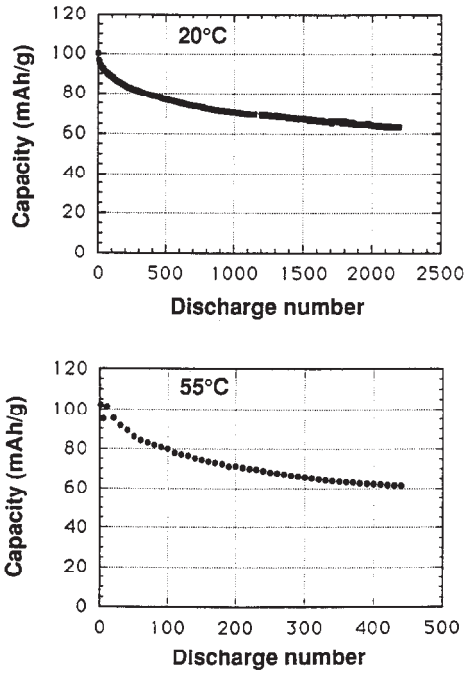


Fig. 12. Variation of the capacity as a function of the cycle number for two $Li_{1+x}Mn_2O_4$/new electrolyte/petroleum coke laboratory test cells operating at 20°C (a) and at 55°C (b).

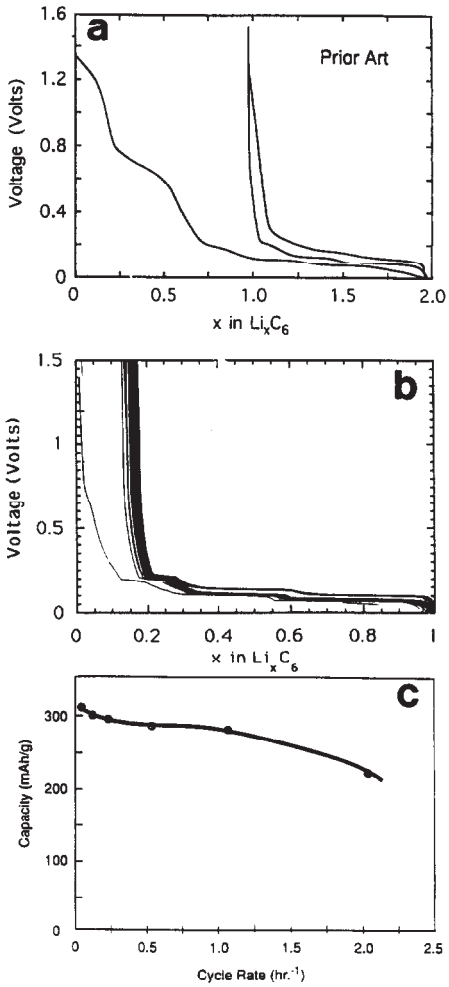


Fig. 13. The previous state of the art for the electrochemical intercalation of Li into graphite is shown in (a). In (b) the typical cyling behavior at 25°C of a graphite/new electrolyte/Li cell charged and discharged at a rated of C/15 is shown with (c) the capacity as a function of various discharging rates for the same cell.

Electrochemical cells using a graphite electrode, 1 M $LiClO_4$-based electrolyte and Li as the negative electrode have shown a high degree of irreversibility during the first cycle (>60%) and poor rate capability. For comparison, the cycling behavior of a cell (denoted cell 1) using our new electrolyte and discharged and charged at C/15 rate is shown in Fig. 13b. Note that the reversibility lost during the first cycle is about 10–15% on the first cycle and then the cell can reversibly intercalate 0.85–0.9 lithiums per formula unit over subsequent cycles. This small reversibility loss implies that the passivating film which forms during the reduction is thin, leading to

the expectation that this electrode should be able to maintain a high current. Figure 13c shows the capacity of this cell as a function of the current. To ensure the absence of Li plating a second identical cell (denoted cell 2) was discharged to lower voltages in order to determine the voltage plateau corresponding to Li plating. For each current the cut-off voltage for cell 1 was always 0.02 V higher that the voltage at which Li plating was occurring as determined by cell 2. Note that the composite electrode maintains at least 90% of its capacity up to C rate. This result indicates that graphite electrodes, when used with this newly discovered electrolyte, not only have a large reversible capacity but can also handle high currents. Because of the increased capacity of the graphite electrode a smaller excess is needed than when petroleum coke is used. By using the three electrode configuration we defined the optimized ratio $Li_{1+x}Mn_2O_4$ vs. graphite to be 2.8.

The electrolyte behavior of rocking-chair cells using the composite graphite electrodes over several cycles is depicted in Fig. 14. After the first five cycles, the cell maintains its capacity over subsequent cycles. Because of the higher ratio (2.8 instead of 2.1 when petroleum coke is used), the cell capacity is increased by 22%. In addition, the lower intercalation voltage of Li into graphite compared to petroleum coke, results in a higher output voltage of the rocking-chair cell (3.8 V instead of 3.7 V). By replacing graphite for coke in our laboratory rocking-chair cells, the overall cell specific energy is increased by 28%.

As a result of our understanding of the electrochemical behavior of laboratory test cells and the optimization of their performance, we have constructed AA research prototype cells using our newly discovered electrolyte cmposition as the ionic media, $Li_{1+x}Mn_2O_4$ as the positive electrode and carbon as the negative electrode (no AA cells using graphite electrodes were built). These AA cells were used for safety and performance evaluations.

All the common safety tests for rechargeable Li batteries were successfully passed. Figure 15a shows the cycling performance of an AA cell. The capacity, initially 0.38 Ah, decreases rapidly during the first few cycles and then levels off at about 0.34 Ah after 50 cycles. The performance of this rocking-chair

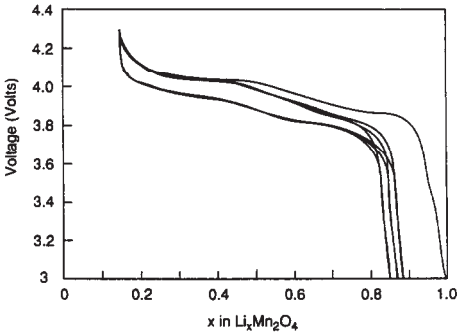


Fig. 14. The voltage–composition curves are shown for an optimized $LiMn_2O_4$/new electrolyte/graphite rocking-chair cell cycled at a rate of C/15 using a weight ratio of positive to negative of 2.9.

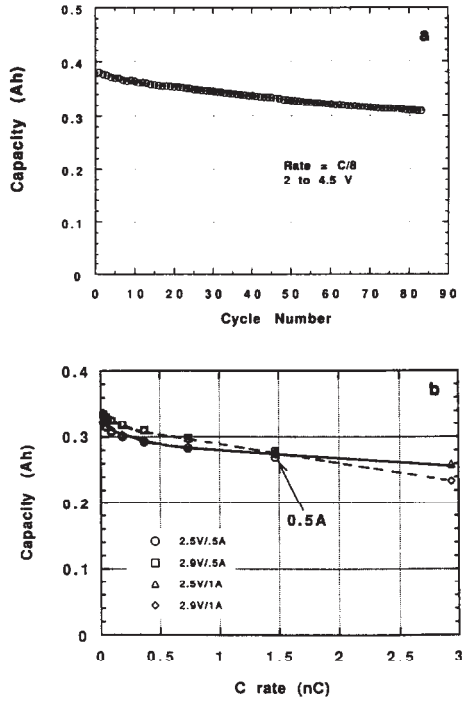


Fig. 15. The capacity of a non-optimized $LiMn_2O_4$ based AA cell is shown as a function of the cycle in (a) while in (b) the ability of the same cell to rapidly deliver energy is depicted.

system is compared to Sony's $LiCoO_2$ system and other battery technologies such as Ni–Cd and Ni–MeH (Table 1). The AA cells were also tested for their rate capabilities. We found that at 1.5 C, these cells can deliver at least 90% of their capacity when discharged to 2.9 V (an important voltage limit for microelectronic applications). The high rate capability of the Mn system could be advantageous not only for discharge but also for rapid recharge of the cell. These unoptimized AA cells showed performances comparable to the Sony cells, and the specific energy density is 1.5 and 2.5 times greater than for similar size Ni–metal hydride and Ni–Cd cells, respectively. As for the laboratory test cells, the replacement of petroleum coke with graphite is expected to further enhance the energy density of these cells by at least 20%. We believe that this

Table 1. The performance of AA research prototype rocking-chair cells based on $Li_{1+x}Mn_2O_4$ as the positive electrode is compared to that of other existing battery technologies

	Capacity	Average voltage	Energy
$Li_{1+x}Mn_2O_4$–C	20.5 Ah kg^{-1}	3.7 V	75 Wh kg^{-1}
AA Prototype	48 Ah l^{-1}		180 Wh l^{-1}
$LiCoO_2$–C	22 Ah kg^{-1}		78 Wh kg^{-1}
AA size	53 Ah l^{-1}	3.6 V	192 Wh l^{-1}
Ni–Cd[33]	25 Ah kg^{-1}		30 Wh kg^{-1}
AA size	72 Ah l^{-1}	1.2 V	87 Wh l^{-1}
Ni–MH[34]	40 Ah kg^{-1}		51 Wh kg^{-1}
AA size	119 Ah l^{-1}	1.26 V	150 Wh l^{-1}

system will be competitive with the $LiCoO_2$ or $LiNiO_2$ Li-ion systems when larger cells are manufactured due to the lower cost of the positive electrode material.

In a very short time, the Li-ion technology has matured and reached a stage where some batteries (Sony for example) have reached the market place and are already powering cellular phones and camcorders. These batteries are being made in AA to D sizes. Larger Li-ion batteries will most likely require connecting in series. A critical issue in that case is that of overcharge protection. Indeed, with aqueous battery systems such as Ni–Cd or Ni–MeH systems, the recombination of decomposed water provides protection in case of overcharge and limits the positive electrode potential. This self-healing mechanism does not yet exist with Li-ion technology. Charging cells in parallel, as opposed in series, is a potential method of mitigating the overcharge problem or using a polymer electrolyte. Thus, efforts in the implementation of polymers in Li-ion cell technology must be maintained and enhanced in view of possible large scale applications. Another way of providing overcharge protection is to include redox shuttle reactants in the electrolyte. Because the $Li_{1+x}Mn_2O_4$ system has a 0.8 V difference between the end of the deintercalation process and the beginning of electrolyte decomposition (in contrast to the $LiNiO_2$ and $LiCoO_2$ systems for which a nonreversible electrolyte decomposition occurs before the end of the intercalation process), the probability of discovering a suitable redox compound is high.

CONCLUSIONS

We have reviewed our study of the rocking-chair type cell based on the spinel $Li_{1+x}Mn_2O_4$ as the positive electrode and carbon as the negative electrode and discussed the critical factors involved in tailoring the electrochemical properties of these materials. We have identified the major hurdles limiting the use of the spinel $LiMn_2O_4$ as the positive electrode and carbon as the negative in a rocking-chair cell and proposed solutions to alleviate them. These include: (1) a novel way of synthesizing non-moisture sensitive $Li_{1+x}Mn_2O_4$ powders; (2) a new electrolyte composition stable against oxidation up to 5 V; and (3) the use of a pure graphite electrode without large irreversible losses. This has led to the construction of AA prototype cells. These cells show enhanced safety characteristics with respect to cells using Li metal as the negative electrode. In addition, they show excellent rate capability and capacity. The performances of the Li–Mn–O based AA cells is similar to other Li-ion cells based on $LiCoO_2$. In general, these cells have an energy density 2.5 and 1.5 times greater than Ni–Cd and Ni–MeH, respectively. Among the three potential rocking-chair systems, the Li–Mn–O based system is the most attractive in terms of cost. This factor will predominate when larger size batteries will be made. Now that the intercalation of lithium into graphite has been achieved successfully, it is difficult to imagine how cheaper materials with better capacity could be found. Finally, cells could be improved by increasing the capacity of the Li-ion cells. This could be achieved by finding positive electrode materials that could reversibly intercalate more than 0.5 Li per metal. However, scientists searching for novel intercalation compounds, must realize that their discoveries will have a practical benefit only if the process as well as the raw materials needed to synthesize this new phases are cheap, in order for the "optimized Li-ion cell" to compete with other existing technologies.

Acknowledgements—The authors are grateful to J. H. Wernick, F. Shokoohi and S. Colson for technical discussions. J. Gural for technical support and want to thank Moli Energy (1990) Ltd. for their willingness to construct AA research prototype cells.

REFERENCES

1. G. Eichinger and J. O. Besenhard, *J. electroanal. Chem.* **72,** 1 (1976).
2. D. W. Murphy and P. A. Christian, *Science* **205,** 651 (1979).
3. J. P. Gabano, *Lithium Batteries*, Academic Press, London (1983).
4. D. P. Wilkinson, J. R. Dahn, U. Von Sacken and D. T. Fouchard, *Papers* 53 *and* 54, 178th *Meeting of the Electrochemical Society*, Seattle, Washington (1990).
5. D. W. Murphy, F. J. DiSalvo, J. N. Carides and J. V. Waszczak, *Mat. Res. Bull.* **13,** 1395 (1978).
6. D. W. Murphy and J. N. Carides, *J. electrochem. Soc.* **126,** 349 (1979).
7. M. Lazzari and B. Scrosati, *J. electrochem. Soc.* **127,** 773 (1980).
8. M. Armand, in *Materials for Advanced Batteries* (Edited by D. W. Murphy, J. Broadhead and B. C. H. Steele), p. 145. Plenum Press, New York (1980).
9. K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, *Mat. Res. Bull.* **15,** 783 (1980).
10. J. J. Auborn and Y. L. Barbario, *J. electrochem. Soc.* **134,** 638 (1987).
11. J. M. Tarascon, *J. electrochem. Soc.* **132,** 2089 (1985).
12. R. Kanno, Y. Takeda, T. Ichikawa, K. Nakanishi and O. Yamamoto, *J. Power Sources* **26,** 535 (1989).
13. M. Mohri, N. Yanagisawa, Y. Tajima, H. Tanaka, T. Mitate, S. Nakajima, M. Yoshida, Y. Yoshimoto, T. Suzuki and H. Wada, *J. Power Sources* **26,** 545 (1989).
14. R. Fong, U. Von Sacken and J. R. Dahn, *J. electrochem. Soc.* **137,** 2009 (1990).
15. T. Nagaura, 4th *International Rechargeable Battery Seminar*, Deerfield Beach, Florida (1990).
16. J. R. Dahn, U. Von Sacken and R. Fong, *Paper* 42, 178th *Meeting of the Electrochemical Society*, Seattle, Washington (1990).
17. J. R. Dahn, U. Von Sacken, H. Al Janaby and M. K. Juzkow, *J. electrochem. Soc.* **138,** 2207 (1991).
18. J. M. Tarascon and D. Guyomard, *J. electrochem. Soc.* **138,** 2864 (1991).
19. D. Guyomard and J. M. Tarascon, *J. electrochem. Soc.* **139,** 937 (1992).
20. D. Guyomard and J. M. Tarascon, in *High Power, Ambient Temperature Lithium Batteries* (Edited by W. D. K. Clark and G. Halpert). Proceedings of the Electrochemical Society, Vol. 92-15, 13 (1992).
21. M. Bartolozzi, *Resources, Conservation and Recycling* **4,** 233 (1990).
22. R. H. Lien, in *Lithium: Current Applications in Science, Medicine and Technology* (Edited by R. O. Bach), Chap. 6. John Wiley, New York (1985).

23. M. M. Thackeray, W. I. F. David, P. G. Bruce and J. B. Goodenough, *Mat. Res. Bull.* **18,** 461 (1983).
24. J. B. Goodenough, M. M. Thackerary, W. I. F. David and P. G. Bruce, *Rev. Chim. Miner.* **21,** 436 (1984).
25. T. Ohzuku, M. Kitagawa and T. Hirai, *J. electrochem. Soc.* **137,** 769 (1990).
26. J. M. Tarascon, E. Wang, F. K. Shokoohi, W. R. McKinnon and S. Colson, *J. electrochem. Soc.* **138,** 2859 (1991).
27. P. Barboux, J. M. Tarascon and F. Shokoohi, *J. Solid State Chem.* **94,** 209 (1991).
28. C. Mouget, Y. Chabre, Multichannel Potentiostat/ Galvanostat "Mac-Pile", licenced from CNRS & UIF Grenoble to Bio-Logic Co, 1 Ave de L'Europe, F-38640 Claix, France.
29. M. M. Thackerary, A. DeKock, and L. A. De Picciotto, *J. Power Sources* **26,** 355 (1989).
30. A. Mosbah, A. Verbaere and M. Tournoux, *Mat. Res. Bull.* **18,** 1375 (1983).
31. J. M. Tarascon, D. Guyomard *et al.* in press.
32. J. R. Dahn, R. Fong and M. J. Spoon, *Phys. Rev. B,* **42,** 6424 (1990).
33. T. Sakai, H. Miyamura, N. Kuriyama and H. Ishikawa, *Paper* 105, 180th *Meeting of the Electrochemical Society*, Phoenix, Arizona (1991).
34. E. Plichta, M. Salomon, S. Slane, M. Uchiyama, D. Chua, W. B. Ebner and H. W. Lin, *J. Power Sources* **21,** 25 (1987).