



the society for solid-state
and electrochemical
science and technology

Journal of The Electrochemical Society

Li Metal-Free Rechargeable $\text{LiMn}_2\text{O}_4/\text{Carbon}$ Cells: Their Understanding and Optimization

D. Guyomard and J. M. Tarascon

J. Electrochem. Soc. 1992, Volume 139, Issue 4, Pages 937-948.
doi: 10.1149/1.2069372

Email alerting service

Receive free email alerts when new articles cite this article - sign up
in the box at the top right corner of the article or [click here](#)

To subscribe to *Journal of The Electrochemical Society* go to:
<http://jes.ecsdl.org/subscriptions>

© 1992 ECS - The Electrochemical Society

ELECTROCHEMICAL SCIENCE AND TECHNOLOGY

Li Metal-Free Rechargeable LiMn_2O_4 /Carbon Cells: Their Understanding and Optimization

D. Guyomard and J. M. Tarascon

Bellcore, Red Bank, New Jersey 07701

ABSTRACT

So-called "rocking-chair" rechargeable batteries that use lithium intercalation compounds for the positive and negative electrodes should be safer than batteries that contain free-lithium metal. Such a cell, using the spinel LiMn_2O_4 as the positive electrode and carbon as the negative electrode, was optimized as a function of various operating parameters. These cells reversibly insert 0.32 Li atoms per Mn at an average output voltage of 3.7 V, yielding an effective specific energy of 250 mWh/g of electrode materials (3 times that of Ni-Cd). They can sustain high current rates similar to Ni-Cd batteries, and can be discharged to 0 V without any degradation of their operating conditions. By systematically studying the stability of several electrolyte systems, we were able to minimize electrolyte decomposition (by controlling drastically the charge cut-off voltage) so that these cells show a promising cycle life even at 55°C while maintaining 75% of their initial capacity.

It is now recognized that ambient temperature non-aqueous secondary lithium cells using lithium metal exhibit problems which make it difficult for their wide usage in the consumer market. These problems are: the short cycle life for deeply discharged cells, the high cost of the technology and, above all, the unsafe operating characteristics due to the high reactivity of lithium metal (1). To alleviate this problem, a "rocking-chair" battery that uses another intercalation compound as the anode has been proposed (2-8). Among the alternative materials that could replace lithium metal as the negative electrode, carbon provides the best compromise between large specific capacity and reversible cycling behavior (9-11). However, a price is paid in terms of average output voltage and energy density as compared to a lithium metal cell, and this is the reason why a strongly oxidizing intercalation compound must be used as the positive electrode. The layered compounds LiNiO_2 and LiCoO_2 and the three-dimensional compound LiMn_2O_4 with the spinel structure, are the only phases presently known to intercalate Li reversibly at voltage larger than 3.5 V vs. Li.

Recently, two battery companies, Moli Energy Ltd. and Sony Energytec Inc. have announced the future commercialization of Li^+ ion rechargeable batteries using a carbon intercalation compound as the negative electrode, and LiNiO_2 and LiCoO_2 or $\text{LiNi}_{0.2}\text{Co}_{0.8}\text{O}_2$ materials as the positive electrodes, respectively (12-14). We also have recently demonstrated the feasibility of such rocking-chair cells using the spinel LiMn_2O_4 and its lithiated parent compound $\text{Li}_2\text{Mn}_2\text{O}_4$ as the positive electrode at 25°C (15).

These rocking-chair batteries do not require a stringent manufacturing environment because the starting electrode materials (i.e. the lithiated manganese oxide and the carbon) are stable in ambient atmosphere. The cell is assembled in its discharged state, where the output voltage is close to 0 V, and, consequently, can be handled before use without any fear of irreversible degradation due to a short circuit. The battery is activated during the first charge. This is similar to the well-known and widely used Ni-Cd batteries that need to be charged prior to their first use.

The use of the spinel manganese oxide material offers the following advantages: LiMn_2O_4 is easy to prepare, compared to the several steps required for the synthesis of LiNiO_2 , and Mn is more abundant and cheaper than Co, so

that the overall electrode cost would be minimized if LiMn_2O_4 is used; The theoretical energy density of LiNiO_2 and LiCoO_2 is twice as high as that of LiMn_2O_4 , but in practice only half of the Li content can be removed, thus leading to the same order of usable energy density for the three materials. Moreover, the energy density of spinel-based manganese oxide cells can be increased if $\text{Li}_2\text{Mn}_2\text{O}_4$ is used (15). The ability to synthesize LiMn_2O_4 at temperatures as low as 400°C (lower than the temperature required to obtain LiNiO_2 and LiCoO_2) also makes this oxide an attractive material for microbatteries compatible with semiconductor technologies (e.g., self-powered electronics). Finally, most of the battery community is already familiar with manganese-based oxides since most of the commercial primary batteries (MnO_2/Li or MnO_2/Zn) use a manganese-based oxide as the positive electrode so that toxicity (if any) or recycling problems are already well known.

The use of a strongly oxidizing compound such as LiMn_2O_4 as the positive electrode is worrisome since the delithiation of this compound occurs at a very high voltage (about 4.1 V vs. Li/Li^+) where the electrolyte oxidation can occur (16). Moreover, such an electrochemical reaction would be accelerated upon increasing the temperature. We have systematically studied the electrolyte oxidation as a function of temperature and the liquid electrolyte used. We succeeded in minimizing the electrolyte decomposition and we show that the LiMn_2O_4 /carbon rechargeable cells can operate at 55°C with good reversibility and without measurable electrolyte oxidation.

This paper details the electrochemical and cycling behavior of the LiMn_2O_4 spinel manganese oxide/carbon rocking-chair cells as a function of various parameters: The ratio of positive and negative electrode masses; The electrode thicknesses; The charge and discharge cut-off voltages; The current and; The operating temperature. We also report the figure-of-merit of these cells as compared to the widely used Ni-Cd battery and to the recently announced Li^+ ion rechargeable battery (13). The electrochemical behavior of each individual LiMn_2O_4 and carbon electrode vs. Li in two different electrolytes will be presented first and separately, with emphasis on the influence of the operating temperature and the voltage limits for cycling. Along with this study, we also have determined the chemical diffusion of Li^+ in the spinel LiMn_2O_4 and in petroleum coke.

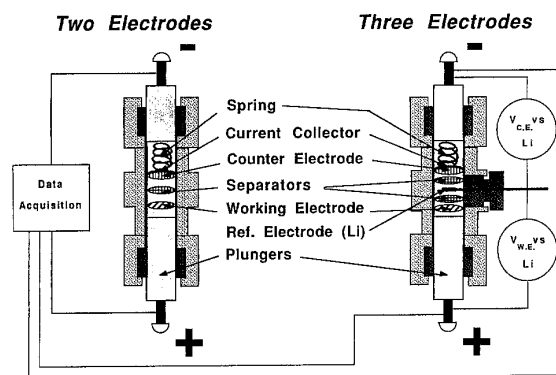


Fig. 1. The drawing of 2 and 3 electrodes Swagelok cells are shown in (a) and (b), respectively.

Experimental

The battery cycling studies presented herein have been made using standard and three electrode Swagelok cells shown in Fig. 1. The plungers were made out of a special stainless steel (Carpenter, Ref. 20Cb-3), that allows oxidative voltages as large as 4.7 V vs. Li without any leakage current due to the electrolyte oxidation. In such cells, the positive electrode (LiMn_2O_4) is in direct contact with the plunger, while the negative electrode (Li or carbon) is in contact with a half-inch diameter nickel disk. Both electrodes are separated by a 0.3 mm thick porous glass paper soaked in the electrolyte selected for the study. To ensure physical contacts between the cell components, a stainless steel spring that allows pressures of about 1 kg/cm² is placed between the nickel disk and the second plunger. In the three electrode design, the reference electrode, a Li foil plated onto a nickel wire sandwiched between two glass paper disks is placed between the positive and negative electrode pellets. These three electrode cells allow the simultaneous *in situ* determination of the three characteristics, V_{positive} vs. Li, V_{negative} vs. Li, and V_{positive} vs. V_{negative} , providing us the information necessary to fully understand, and optimize, the behavior of these secondary cells. For the cyclic voltammetry measurements, a three electrode glass cell, consisting of a working electrode, a reference electrode (piece of lithium foil plated onto a nickel wire), and a counterelectrode (made the same way as the reference electrode) was used. The working electrode was either a glassy carbon electrode (to study the oxidation limit of some electrolytes) or a pellet of tested material compacted onto a platinum gauze (for the electrochemical characterization of this material). Both the Swagelok cells and the three electrode glass cell were always assembled in a helium atmosphere. Then, the air-tight Swagelok cells were removed from the dry box to be tested. No loss of electrolyte was detected for these cells even after a series of tests at 55°C during 1 month.

LiMn_2O_4 materials were prepared by reacting in air stoichiometric amounts of Li_2CO_3 and MnO_2 placed into an alumina crucible. In accordance with our previous work (17), because of their larger capacity, LiMn_2O_4 powders (1 to 2 μm particle size) prepared by three consecutive anneals at 800°C (24 h each) were used as the positive electrodes. Petroleum coke (Conoco, -200/400 mesh; i.e. particle size between 38 and 75 μm) was used instead of graphite as the negative electrode, because of a lower loss of capacity compared to graphite at the first cycle, although its capacity is twice as small (its maximum Li composition has been reported to be $\text{Li}_{0.5}\text{C}_6$ instead of LiC_6 (18, 19)). Composite electrode materials containing the active material, carbon black, and EPDM (ethylene propylene diene monomer) rubber were made by mixing the powders in a solution of EPDM in cyclohexane, evaporating the solvent, sieving the resulting powders to 100 μm and pressing them at a pressure of 10 tons/cm² into pellets. The resulting composite material will be denoted by three numbers [a, b, c] where a, b, and c will refer to the weight ratio of the active material, carbon black, and EPDM, re-

spectively, (for example a composite electrode containing 90% LiMn_2O_4 , 8% carbon black, and 2% EPDM will be denoted as [90, 8, 2]). A survey of several compositions was done for both composite electrodes in order to optimize the cyclability performance of the composite electrodes with respect to Li. The results of such a survey show that the compositions [89, 10, 1] and [94, 5, 1] give the best reversibility vs. Li for the positive and negative electrodes, respectively, as well as the lowest polarization (minimum difference in voltage between charge and discharge curves). These compositions were used in all the results reported here. Although thermogravimetric analysis measurements (TGA) of the composite electrodes did not reveal any trace of water, all the electrodes were heated at 150°C during 1 h, prior to being used as electrodes in rocking-chair batteries to eliminate any possibility of water contamination. For all the cells using LiMn_2O_4 as the positive electrode, we took the Li content $x = 1$ as the initial stoichiometry, and then the composition was automatically determined from the current, the mass of the active cathode material used, and the elapsed time. From the values of x , the equivalent capacity in mAh/g reported in several figures is simply obtained by multiplying the theoretical capacity 148.2 mAh/g by Δx .

Propylene carbonate (PC), with its low vapor pressure and high flash point, was used for the solvent. To increase the ionic conductivity of an electrolyte without changing the nature and content of the salt, mixtures of solvents are generally used. For instance, high dielectric constant solvents like ethylene carbonate (EC) or PC are mixed with low dielectric constant and low viscosity solvents (like 2-methyl-tetrahydrofuran (2Me-THF) or dimethoxyethane (DME)) (20). In this study, diethoxyethane (DEE) was selected instead of the commonly used 2Me-THF or DME, because its boiling point is higher (121°C compared to 80°C), thereby limiting safety hazards (e.g., explosions) and the solvent mixture consisting of EC and DEE, 50-50 by weight, was tried. The solvents (Aldrich) were dried using standard methods. For EC and PC, the solvents were degassed by 3 pump/refill cycles using Ar as the inert gas. EC was warmed to above the melting point. The solvents were dried over 4 Å molecular sieves for 48 h and then were distilled under reduced pressure (15 Torr). DEE was degassed by 3 freeze-pump-thaw cycles, and was distilled under Ar from K benzophenone ketyl.

Different electrolytes have been made by adding various widely used Li salts (heat-vacuum dried prior to their use), such as LiAsF_6 , LiCF_3SO_3 , LiBF_4 , LiPF_6 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, and LiClO_4 to PC or EC + DEE (50:50). After the drying process, the x-ray powder diffractograms were controlled to exclude any possibility of degradation. The best Li-salt, defined in this study as the one allowing the largest electroactivity range at high voltage, was selected as follows. First, the oxidation limit of the electroactivity range of these electrolytes has been determined by cyclic voltammetry on a glassy carbon electrode. The oxidation current of the electrolytes is located in the range 4.6 to 5.0 V vs. Li, showing that all these salts could be used up to a voltage of 4.5 V vs. Li in any battery. This measurement, however, is not fully indicative since it does not reflect the true operating conditions because, the catalytic activity of any positive electrode material could be different from that of the glassy carbon, and the standard scan rate used for metal electrodes (0.1 V/s) is much higher than that used for cycling an intercalation electrode material (10^{-4} to 10^{-5} V/s). Thus, these different electrolytes have been tested under real operating conditions in LiMn_2O_4 /electrolyte/Li cells up to 4.5 V and the salt allowing for largest charge cut-off voltage on the LiMn_2O_4 material, over a large number of cycles without any oxidation of the electrolyte, is LiClO_4 . Other salts can also be used with LiMn_2O_4 , but they allow a smaller electroactivity range. Consequently, from this study, the two electrolytes PC + 1M LiClO_4 and EC + DEE (50:50) + 1M LiClO_4 were selected and Fig. 2 shows their oxidation limit measured by cyclic voltammetry at the two temperatures used in this work. The PC-based electrolyte allows higher voltage values, but for both electrolytes the oxidation limit is lowered by 0.2 V when the operating temperature is increased to 55°C.

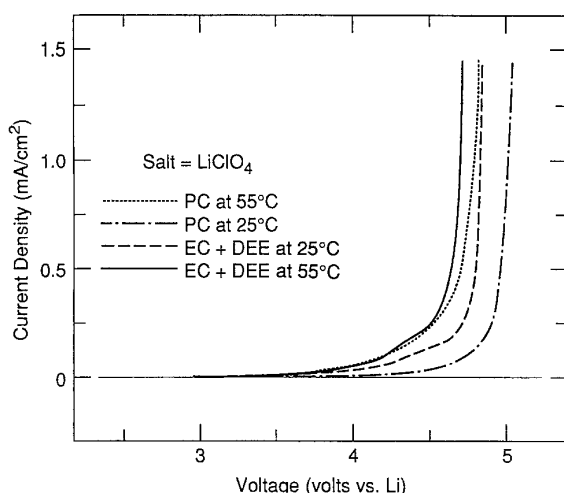


Fig. 2. Cyclic voltammograms at glassy carbon electrode of EC + DEE (50:50) + 1M LiClO₄ and PC + 1M LiClO₄ electrolytes at 25 and 55°C. Scan rate = 0.1 V/s.

The ionic conductivity and the water content for the selected electrolytes used for our experiments were determined using a high frequency impedance analyzer and a Karl-Fisher coulometer, respectively. Ionic conductivity values of 10.4 and 5.62 mS/cm at room temperature (25°C) and water contents of 45 and 40 ppm were obtained, for the two electrolytes EC + DEE (50:50) + 1M LiClO₄, and PC + 1M LiClO₄, respectively.

The chemical diffusion coefficients of Li⁺ ions in both LiMn₂O₄ and carbon electrodes were measured using the potentiostatic intermittent titration technique (PITT) (21, 22) by means of a special multichannel galvanostatic/potentiostatic system "Mac-Pile." In this system the potentiostatic mode acts as a coulometer so that the experimental parameter is the charge increment *vs.* time and not the current *vs.* time as usually measured. Thus, in our experiment, the potential of the material/Li cell is monitored by steps, and the decay of the charge increment (the integral of the current) during each step is measured as a function of time. The resolution of Fick's second law for times $t \ll l^2/D$ and $t \gg l^2/D$ leads to the Eq. [1] and [2], respectively, for the variation of the charge increment as a function of time

$$q(t) = \frac{2FSD^{1/2}\Delta C}{\pi^{1/2}} \sqrt{t} \quad [1]$$

$$q(t) = \frac{8FSI\Delta C}{\pi^2} \exp\left(-\frac{\pi^2 Dt}{4l^2}\right) \quad [2]$$

where t is the elapsed time from the beginning of the step, F is the Faraday constant, S is the total surface area of the grains of the active material, ΔC is the variation of Li concentration into the material during the voltage step, D is the chemical diffusion coefficient of Li⁺ into the material, and l is the size of the material grains. The chemical diffusion coefficient D of Li⁺ can then be determined by the slope of the linear plot of q *vs.* $\sqrt{t}$ in the short time approximation, and by the slope of the linear plot of $\log q$ *vs.* t in the long time approximation. The accuracy of this technique directly depends on the evaluation of the total surface area. In this work, we have estimated this surface area by assuming that the grains are spherical with a diameter equal to the average particle size.

Results and Discussion

Behavior of LiMn₂O₄ *vs.* Li.—Figure 3a shows the room temperature cycling behavior of a LiMn₂O₄/Li cell under constant current in the two electrolytes, EC + DEE (50:50) + 1M LiClO₄ and PC + 1M LiClO₄. The cell is first charged from its rest voltage (close to 3.3 V *vs.* Li) to 4.5 V

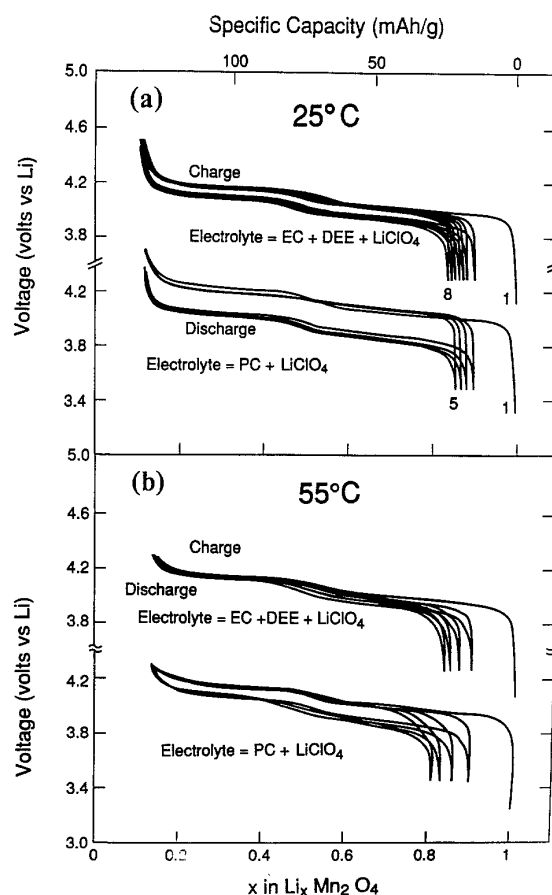


Fig. 3. Typical cycling behavior at 25 (a) and 55°C (b) of LiMn₂O₄/Li cells using EC + DEE (50:50) + 1M LiClO₄ and PC + 1M LiClO₄ electrolytes. In (a) the cells contain 30 mg (of active material) and were cycled between 3.5 and 4.5 V at a current of 0.4 mA/cm² ($\Delta x = 1$ in 22 h). In (b) the cells contain 10 mg (of active material) and were cycled between 3.5 and 4.3 V at a current of 0.2 mA/cm² ($\Delta x = 1$ in 15 h).

vs. Li. The removal of one Li⁺ from the structure (leading to λ -MnO₂) occurs in two steps close to 4.1 V *vs.* Li as shown in previous work (17, 23-26). On discharge, λ -MnO₂ converts back reversibly to LiMn₂O₄ in two steps. Independently of the electrolyte used, the material shows the same reversible capacity after the first charge-discharge cycle, $\Delta x \approx 0.8$, corresponding to 119 mAh/g of active material. The loss in capacity during the first cycle ($\Delta x \approx 0.2$) may arise from particles that become electrically disconnected and also results from the fact that the battery is cycled under constant current without any relaxation so as to allow the system to reach equilibrium upon Li⁺ intercalation. For composite LiMn₂O₄ electrodes of the same thickness, the polarization ($V_{\text{charge}} - V_{\text{discharge}}$) is about three times lower in the EC- than in the PC-based electrolyte (Fig. 3a), consistent with the higher ionic conductivity measured for the EC- than the PC-based electrolyte.

In order to determine the maximum voltage to which rechargeable Li cells based on LiMn₂O₄ as the positive electrode can operate safely, we have tried several cut-off voltages on charge. Figure 4 shows what happens if the charge cut-off voltage of a LiMn₂O₄/Li cell is increased after a few cycles. A plateau is obtained at 4.59 V *vs.* Li, corresponding to an irreversible electrochemical reaction. As a result, the next discharge curve is shifted to lower values of x , with a value corresponding to the capacity length of this plateau. This reaction could be the oxidative degradation of the λ -MnO₂ framework or the oxidation of the electrolyte at the surface of the material. The x-ray diffraction pattern of the sample after this treatment shows no difference

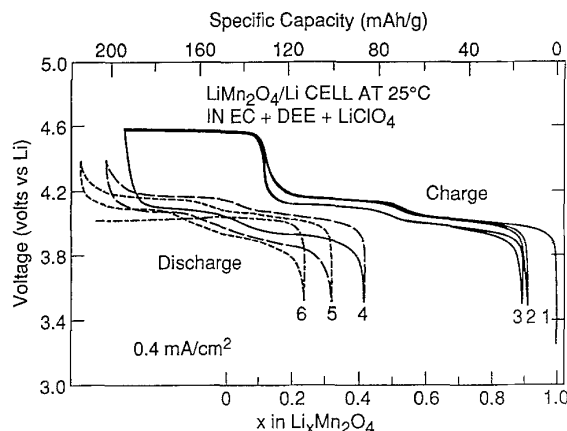


Fig. 4. Cycling behavior at 25°C of a $\text{LiMn}_2\text{O}_4/\text{Li}$ cell in EC + DEE (50:50) + 1M LiClO_4 when the charge cut-off voltage is increased above 4.5 V. The pellet was 30 mg (active material) and a current rate of 0.4 mA/cm^2 was used ($\Delta x = 1$ in 22 h). The charge cut-off voltage was 4.5 V for the 2 first charges, then 4.6 V for the third charge, and then 4.4 V for the following charges. The discharge cut-off voltage was always 3.5 V.

with the one for $\lambda\text{-MnO}_2$, excluding the first possibility. In an attempt to avoid further oxidation of the electrolyte, the following charges were limited to 4.4 V vs. Li. However, at each successive cycle, even if the voltage is kept lower than 4.4 V vs. Li, the voltage-composition curves show lower capacity and larger polarization than a cell that has not been charged above 4.5 V vs. Li. In addition, these curves are shifted to larger capacity values, due to some irreversible behavior coming from the oxidation of the electrolyte. After a few cycles, the high voltage cannot be reached and the delithiation of the spinel no longer occurs (e.g. the cell cannot be used any longer). These results indicate that once the oxidation of the electrolyte has been initiated by an increase in cut-off voltage, its decomposition voltage is lowered into the cycling window so that it cannot be stopped even by lowering the cut-off voltage on subsequent cycles. This emphasizes the importance of carefully controlling the overvoltage in charging these cells: 4.45 V vs. Li is a safe limit at room temperature that allows one to use the whole capacity without risk of electrolyte decomposition.

The behavior of the LiMn_2O_4 material at high voltage has been studied further by cyclic voltammetry at room temperature. The three electrode technique allows one to study only the contribution of the LiMn_2O_4 /electrolyte interface and consequently avoid any phenomenon occurring at the Li electrode or any secondary reaction susceptible to occur at the metal current collector in Swagelok test cells. The voltammograms of Fig. 5 show two peaks in oxidation and two peaks in reduction, when the electrode material is cycled between 3.3 and 4.45 V vs. Li, which are the signature of the two-step reversible transformation between LiMn_2O_4 and $\lambda\text{-MnO}_2$ (17, 21-23). If the higher voltage limit is increased above 4.5 V vs. Li, an oxidation current appears on the anodic scan direction. On the following cathodic scan, above 4.5 V vs. Li, this current is always oxidative, so it leads to irreversible capacity. This current is intrinsic to the material, due to oxidation of the electrolyte on the electrode material surface, because the oxidation of the electrolyte on the Pt holder remains slow in the same voltage range (dot-dashed line in Fig. 5). On the subsequent cycles, the current peaks become larger and badly defined, in contrast to that observed if the voltage is always kept below the limit 4.5 V vs. Li. This degradation of the behavior of the manganese oxide could be due to the deposition of an insulating layer, composed of the products of the electrolyte oxidation, at the surface of the grains. Comparing the curves obtained in both electrolytes, we see that the voltage separation between the peaks in the oxidation scan direction and in the reduction scan

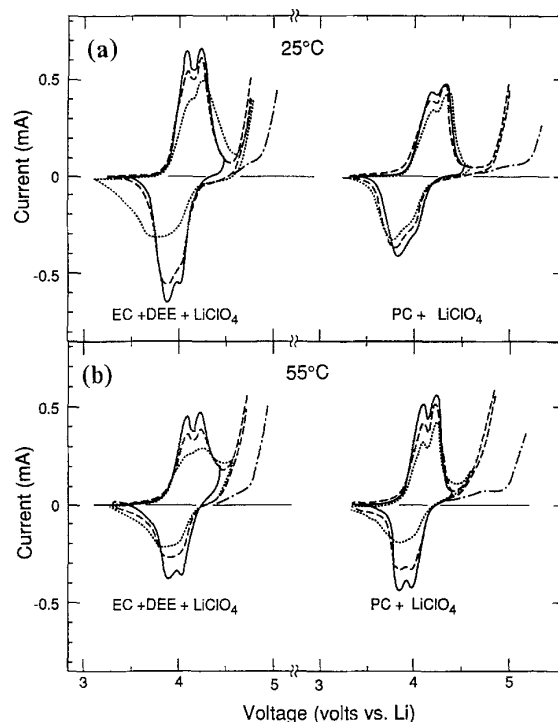


Fig. 5. Cyclic voltammograms at LiMn_2O_4 in EC + DEE (50:50) + 1M LiClO_4 and PC + 1M LiClO_4 electrolytes at 25°C (a) and at 55°C (b). For all the voltammograms the starting voltage is close to 3.2 V and the scan rate is of 0.1 mV/s. The solid line, dashed line and dot line refer to the 1st, 2nd, and 4th cycle, respectively, while the dot-dashed line is obtained as a blank on the Pt grid holder alone until very high voltage is used. For the voltammograms (a) the voltage is first scanned to 4.45 V and back to 3.3 V (solid line) and then to 4.75 (for EC-based electrolyte) or 4.95 V (for PC-based electrolyte) for following sweeps in the positive direction. For the voltammograms (b) the voltage is first scanned to 4.42 (for EC-based electrolyte) or 4.37 V (for PC-based electrolyte) and back to 3.2 V (solid line) and then to 4.7 (for EC-) or 4.85 V (for PC-) for following sweeps in the positive direction.

direction (e.g., the polarization) is lower in EC- than in PC-based electrolyte, because the ionic conductivities of the two media are different. Moreover, the oxidation of the electrolyte on the material surface occurs at a lower voltage and the degradation of the shape of the voltammograms occurs faster in the EC-based electrolyte. From this study, we conclude that the degradation of the reversible cycling behavior of the LiMn_2O_4 material after an overcharge exceeding 4.5 V vs. Li is intrinsic to the LiMn_2O_4 /electrolyte interface and arises from the electrolyte oxidative decomposition at the surface of the material grains.

Another important question to be addressed is what happens at higher operating temperature where a battery operates in practice. Figure 3b shows the cycling behavior of $\text{LiMn}_2\text{O}_4/\text{Li}$ cells at 55°C under constant current in the two electrolytes we selected. Note that a lower charge cut-off voltage than the one used at room temperature (4.3 V vs. Li instead of 4.5 V vs. Li) was sufficient to obtain the complete capacity. Again, the polarization is greater in PC- than in EC-based electrolytes but less than that observed at room temperature, as expected, because of an increase in the ionic diffusion rate with increasing temperature. The loss of capacity during the first few cycles is slightly larger than at room temperature, and is slightly larger in PC- than in EC-based electrolytes.

The same cyclic voltammetry study as was done at room temperature shows that at 55°C the electrolyte oxidation limit is effectively lowered by about 0.2 V in EC and 0.25 V in PC (Fig. 5b). As observed at room temperature the electrolyte oxidation still occurs at a higher voltage in PC than

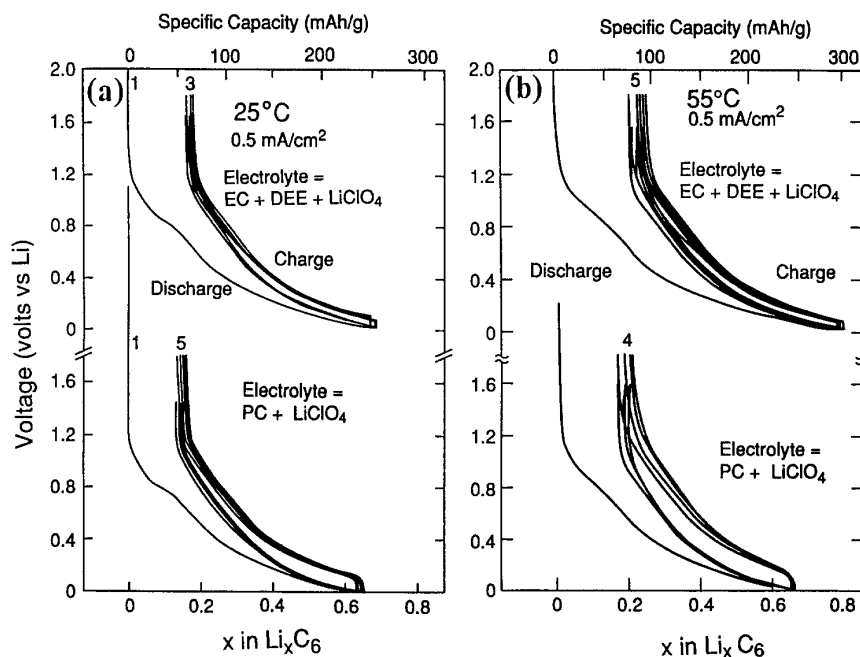


Fig. 6. Typical cycling behavior at 25°C (a) and at 55°C (b) of carbon (petroleum coke)/Li cells using the electrolytes EC + DEE (50:50) + 1M LiClO_4 and PC + 1M LiClO_4 . All the cells contain 30 mg (of active material) and are cycled between 0.02 V and 1.8 V at a current of 0.5 mA/cm² ($\Delta x = 0.5$ in Li_xC_6 was obtained in 22 h).

EC, and the polarization is always higher in PC than in EC. Compared to what happened at room temperature, the degradation of the cycling behavior of the cell occurred faster. Note that at 55°C, using a scan rate of 0.1 mV/s, corresponding to a charge-discharge cycle of the manganese oxide of less than 2 h instead of 18 h under galvanostatic control (Fig. 3) the current trace in EC (Fig. 5b) does not reach a low value at 4.5 V vs. Li suggesting that the oxidation of the electrolyte begins before the end of the delithiation of the spinel. However, at such high scan rates the width of the peaks are larger and, equivalently, the electrochemical reactions occur in a larger voltage range. The use of an adequate charge cut-off voltage (4.3 V vs. Li in the present conditions), will avoid the electrolyte oxidation and yet still allow an acceptable capacity for the deintercalation reaction.

From this study and the study of the cycling behavior of $\text{LiMn}_2\text{O}_4/\text{Li}$ cells under constant current, we conclude that the degradation of the electrolyte begins at a voltage far enough from the delithiation voltage of the spinel, so that LiMn_2O_4 can be used as a positive electrode, even for cells operating at 55°C.

Behavior of carbon vs. Li.—Figure 6a shows the cycling behavior at room temperature of a carbon (petroleum coke)/Li cell under constant current in the two electrolytes EC + DEE (50:50) + 1M LiClO_4 and PC + 1M LiClO_4 . The cell is first discharged from its rest voltage (usually in the range 3.0 to 3.3 V vs. Li) to 0.02 V vs. Li. The intercalation of Li^+ ions in the structure occurs without the formation of any staged-phase because of the lack of crystalline order of the material, as was shown in previous work (11, 18). The charge is much shorter than the first discharge, but the following cycles show excellent reversibility over $\Delta x = 0.5$ in Li_xC_6 , corresponding to 186 mAh/g of active material. The large irreversible capacity loss after the first cycle has been attributed to the formation of a passivating film at the grain surfaces, often called solid electrolyte interface (SEI), arising from the reduction of the solvent at a voltage lower than 1.2 V vs. Li (18). On the following cycles, this passivating layer protects the carbon from any direct contact with the electrolyte, preventing its further reduction and allowing only for the Li intercalation-deintercalation reaction. This loss in capacity during the first cycle is almost the same in EC (23%) and in PC (21%), but the polarization is twice as high in PC than in EC.

The voltage composition traces for a carbon/Li cell operating at 55°C is shown in Fig. 6b. This behavior is very sim-

ilar to that at room temperature. However, the irreversibility at the first discharge is slightly higher than at room temperature (27% instead of 23% in EC + DEE (50:50) and 25% instead of 21% in PC) while the capacity loss during the 5 first cycles is slightly higher than at room temperature. The reversible capacity in EC + DEE (50:50) + 1M LiClO_4 at 55°C is found to be $\Delta x = 0.55$ in Li_xC_6 , about 10% higher than what is observed at room temperature.

The voltage limits, in which the carbon electrode can work properly, have been studied carefully. The Li^+ ions are completely removed from the carbon electrode at a voltage higher than 1.5 V vs. Li, but the charge can be increased until 3.9 V vs. Li with negligible excess capacity and without affecting the reversible behavior upon cycling, because 1.5 to 3.9 V is an electrochemically inactive voltage range for carbon. Figure 7a shows the first cycle down to very low voltage of a carbon/Li cell obtained using periodic times of constant current and relaxation under open circuit. The cell has been discharged to -0.045 V vs. Li under current, with a relaxation open-circuit voltage always positive vs. Li. No change in the slope of the voltage-composition curve is observed, indicating that over this range of potential the intercalation of Li^+ ions into the carbon structure is the only electrochemical process occurring. A negative voltage vs. Li is meaningless. In fact, the intrinsic voltage is always positive, as expected, but the IR term (R being the internal resistance of the cell and I the current flow) always adds to the intrinsic voltage and gives a negative measured value. The negative voltage limit used here depends strongly then on the experimental conditions through the term IR (e.g., R increases with the thickness of the pellet). The structural changes in the carbon during this deep discharge were followed using an *in situ* x-ray cell over the range of 2θ corresponding to the [002] Bragg peak whose changes in position directly reflect changes in the spacing between two consecutive graphite layers. The width at half maximum of this diffraction peak was found to remain constant during the cell discharge in contrast to its position. Figure 8 shows that the interlayer distance $d(002)$ varies continuously as a function of x in the range $0 < x < 0.7$, confirming that Li intercalation is the only phenomenon occurring in this voltage range. When the cell is recharged the [002] Bragg peak converts back to its original position indicating further that the intercalation process is reversible over this range of composition and voltage. These results show that 0.7 Li can be intercalated reversibly in Li_xC_6 , resulting in an increase of the mean interlayer distance from 3.47 to 3.77 Å. To our knowl-

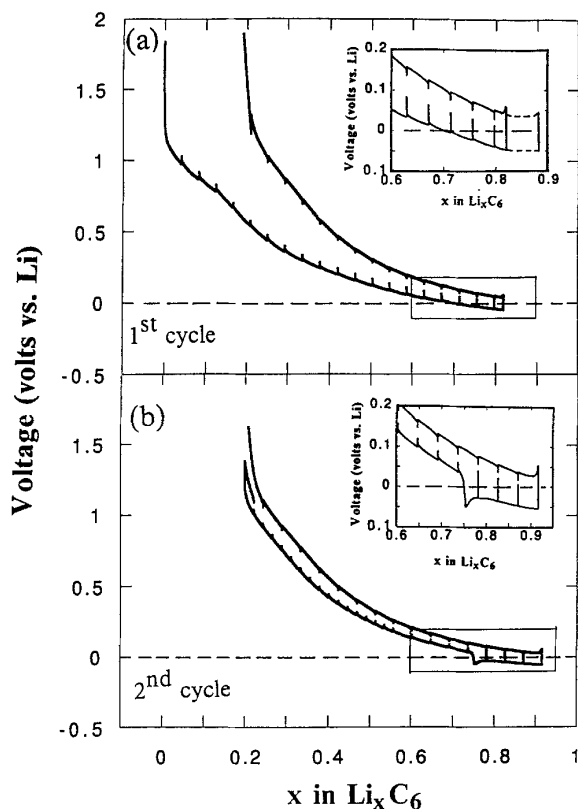


Fig. 7. The first and second cycles obtained at room temperature when discharging a carbon (petroleum-coke)/1M LiClO₄ in EC + DEE (50:50)/Li cell to -0.045 V vs. Li are shown in (a) and (b), respectively. The data were obtained by applying to the cell charging or discharging current pulses of 0.5 mA/cm^2 for 2 h with a relaxation time of 1 h between two consecutive pulses. The thickness of the carbon pellets are 0.45 mm and they contain 30 mg of active material. As a help to the reader the low voltage part of the $V(x)$ curves are enlarged (see inserts).

edge, this is the maximum range of reversible lithium intercalation reported for petroleum-coke. If carbon is discharged to -0.05 V vs. Li, then a plateau appears in the voltage-composition curve and the relaxation open-circuit voltage is very close to 0 V; this plateau corresponds to Li plating, as indicated by the interlayer distance that remains constant. When a carbon/Li cell is discharged-charged several times to -0.05 V, we note during the second discharge and each subsequent discharge the presence of an anomaly located at 0.02 V in the discharge curve (Fig. 7b). Although not present during the charge of the cell, this anomaly (seen after the second cycle in all the carbon/Li cells discharged below 0.02 V vs. Li) does not appear to affect the reversibility of these cells. We presently have no qualitative explanation to account for such an anomaly. Li plating cannot explain it since we previously demonstrated that the voltage plateau for lithium plating occurs at quite lower voltages (below -0.04 V). Similarly, an underpotential deposition of Li metal on the current collectors can be ruled out because such a process should lead to a kind of pseudo-plateau in the voltage-composition curve, instead of a drop as experimentally observed.

To fully capitalize with the range of reversibility of the negative carbon electrode one needs to operate at voltages close to Li plating, which is undesirable for safety reasons. For this reason, in this work we chose to limit the discharge of carbon to the composition $\text{Li}_{0.5}\text{C}_6$ (that corresponds to a voltage limit of 0.02 V vs. Li under the present experimental conditions) to allow a safe voltage range before the deposition of free Li metal. In addition, in this composition range, the voltage-composition curves for a

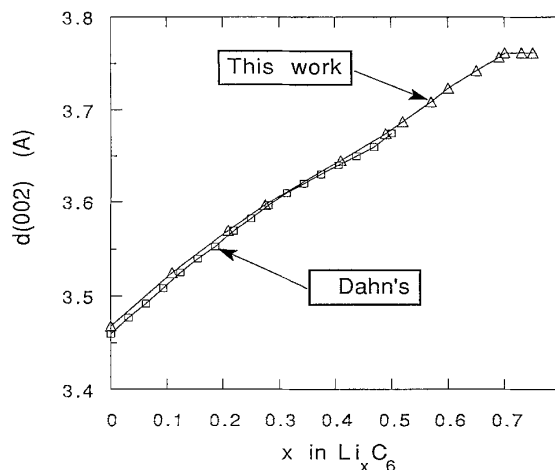


Fig. 8. The variation of the interlayer spacing between the graphite layers for petroleum-coke upon Li intercalation is shown together with the results previously published by Dahn *et al.* (11). The data were taken during the second discharge at a current rate of $20 \mu\text{A/cm}^2$ of a cell containing 4.5 mg (active weight) of carbon.

carbon/Li cell are not affected by the anomaly previously described. The advantage of using fully lithiated petroleum-coke ($\text{Li}_{0.7}\text{C}_6$) in terms of increasing the energy density of rocking-chair cells will be briefly mentioned.

Determination of the chemical diffusion coefficients of Li^+ ions in LiMn_2O_4 and carbon.—The cycling behavior of both electrodes vs. Li has shown a low polarization between charge and discharge, even at relatively high current, suggesting that the kinetics of the lithium intercalation process in both LiMn_2O_4 and C is not slow. To further address this point, the chemical diffusion coefficients of Li^+ in both electrodes at room temperature were determined by PITT experiments. For each electrode material the measurements were collected during the second cycle to avoid the influence of any irreversible phenomenon occurring during the first cycle. Diffusion coefficients have been determined for $\lambda\text{-MnO}_2$ and the $\text{Li}_x\text{Mn}_2\text{O}_4$ single phase region ($0.5 \leq x \leq 1$) (25). Our data show that the variation of q as a function of $\sqrt{t}$ is perfectly linear in the short time range.

The D values, calculated from the slope of the lines, are presented in Fig. 9a. It is important to note that the diffusion coefficients of Li^+ ions in the positive electrode material $\text{Li}_x\text{Mn}_2\text{O}_4$ are independent of the composition x at least until $x = 1$, with a value in the order of $10^{-9} \text{ cm}^2/\text{s}$. Similarly, the diffusion coefficients of Li^+ ions have been determined for the whole range of composition in petroleum coke. We observed a faster diffusion coefficient for Li^+ ions (Fig. 9b) with D values that decrease almost linearly from $10^{-8} \text{ cm}^2/\text{s}$ to $10^{-9} \text{ cm}^2/\text{s}$ during the intercalation.

These results confirm a reasonable mobility of Li^+ ions in both LiMn_2O_4 and carbon, leading to the expectation that rocking-chair batteries using both materials as electrodes could sustain high current as will be demonstrated.

Behavior of the LiMn_2O_4 /carbon cell.—A rocking-chair cell contains an intercalation compound for both the positive and negative electrodes. To optimize its electrochemical performance, *i.e.*, determine the eventual cause of failure in these cells and optimize their capacity, one must know the chemical potential of Li^+ ion in each electrode material during the cycling of the cell, which is given by the voltage profile of each electrode vs. Li. A three electrode Swagelok cell (Fig. 1), with Li as the third electrode was used for the *in situ* determination of the three characteristics $V_{\text{positive vs. Li}}$, $V_{\text{negative vs. Li}}$, and $V_{\text{positive vs. negative}}$. The two first curves allow one to understand what happens in each electrode while the rocking-chair cell is cycled, and the third one is the output voltage of the battery.

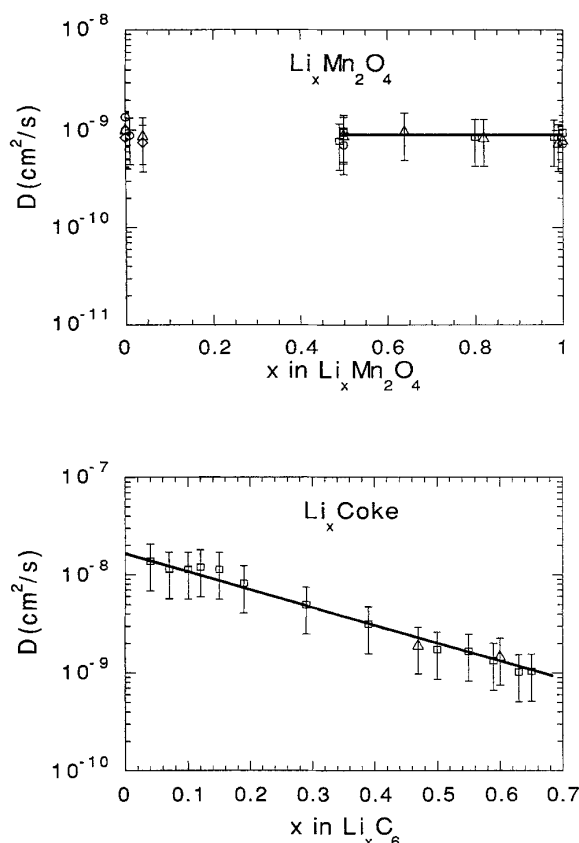


Fig. 9. The room temperature variation of the chemical diffusion coefficient of Li^+ as function of composition (x) in the spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ and in petroleum coke Li_xC_6 is shown in curves (a) and (b), respectively. For curve (a) steps of either 10 mV every 10 h or 5 mV every hour were used for the first discharge and second charge/discharge cycle. For curve (b) steps of 10 mV every 2 h were used.

Optimization of the electrode mass ratio.—When a rocking-chair cell made with LiMn_2O_4 and carbon intercalation compounds is charged, the Li^+ ions deintercalate from the Li-bearing positive electrode and intercalate into the negative electrode. Thus, the amount of electrode materials are directly correlated. As a first estimate of the best ratio $r = m_+/m_-$ of positive and negative electrode masses, we take the value that gives equal capacities for the first discharge of Li_xC_6 vs. Li to 0.02 V (Fig. 6a) and the first charge of LiMn_2O_4 vs. Li to 4.5 V (Fig. 3a). This optimum value of r is supposed to correspond to a cell where the LiMn_2O_4 electrode is fully deintercalated when the negative carbon electrode reaches the safe voltage limit of 0.02 V vs. Li metal. This estimate gives r -values of 1.95 and 1.87 for EC- and PC-based electrolytes, respectively, at room temperature. But these values are based on two-electrode cells, with no correction for polarization at the Li electrode.

We made a three-electrode cell with $r = 1.9$, and found that the masses were not optimally balanced at the end of the first charge; the LiMn_2O_4 is completely deintercalated, but the voltage of the carbon electrode is well above 0.02 V vs. Li. To refine the value of r further, we made a series of three-electrode cells with different values of r , with the results shown in Fig. 10 and Fig. 11. When r increases (Fig. 10), the curves are shifted toward higher voltages with slightly increased capacity. As a matter of fact, when r increases, for a given mass of positive electrode the mass of negative electrode decreases, leading to lower carbon voltages vs. Li and, consequently, larger output voltage of the battery. Using a large r ratio is attractive because it improves the battery performance, but if too large, one runs into the risk of Li plating on the carbon electrode, as illustrated in Fig. 11. In general, for values of r greater than 2.2

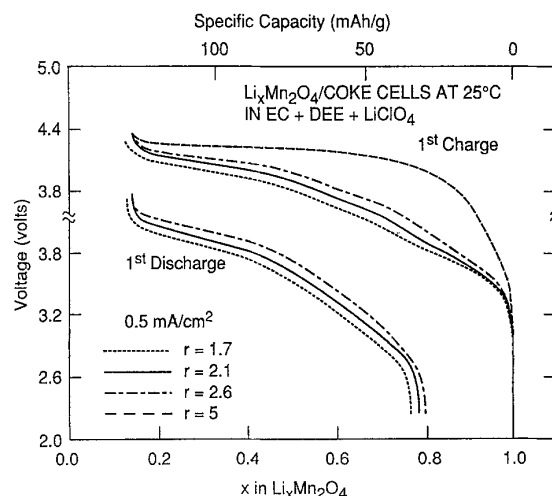


Fig. 10. The first cycle (charge and discharge) at 25°C of $\text{Li}_x\text{Mn}_2\text{O}_4$ /carbon (petroleum coke) cells made with different ratios $r = m_+/m_-$ of electrodes masses. The electrolyte is EC + DEE (50:50) + 1M LiClO_4 . The carbon mass is always 30 mg and the current 0.5 mA/cm^2 ($\Delta x = 0.5$ in Li_xC_6 was obtained in 22 h). The voltage limits were 2.3 and 4.35 V (for all the r but 1.7) or 4.3 V (for $r = 1.7$).

the carbon electrode reaches a voltage below 0.02 V vs. Li and a composition in Li greater than 0.5 per formula unit ($\text{Li}_{0.5}\text{C}_6$). More specifically, if $2.2 < r \leq 2.6$, only Li intercalation into carbon occurs without Li plating ($r = 2.6$ allows reaching the composition $\text{Li}_{0.7}\text{C}_6$ when the LiMn_2O_4 is fully delithiated). While if $r > 2.6$, then the carbon voltage-composition curve reaches a plateau with negative voltage, corresponding to Li plating, before the end of the delithiation of the manganese oxide. On the contrary, at r values smaller than 2 (Fig. 11), the rocking-chair cell appears to have an excess of carbon material because the intercalation of Li^+ into the carbon is not completed ($V > 0.2$ V vs. Li) at the end of the delithiation of the manganese oxide.

The optimized r value is about 2.1 at room temperature (Fig. 11), because at the end of the first charge ($V = 4.35$ V), the positive electrode is completely delithiated with a composition corresponding to $\lambda\text{-MnO}_2$ at a voltage far enough from the electrolyte oxidation ($V = 4.37$ V vs. Li).

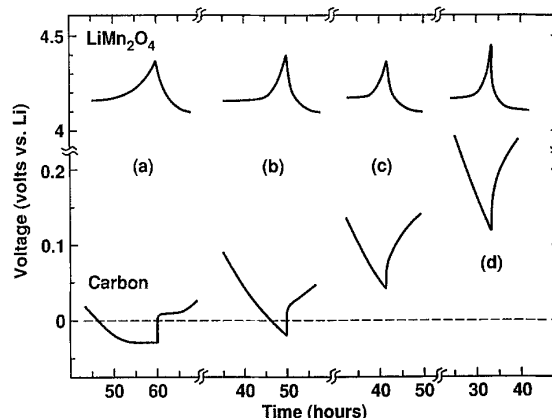


Fig. 11. Voltage profiles vs. Li of LiMn_2O_4 and carbon (petroleum coke) electrodes at the end of the first charge and the beginning of the first discharge when different ratios $r = m_+/m_-$ of electrodes masses are used but always with the same mass of carbon (30 mg) and the same current (0.4 mA/cm^2). The letters a, b, c, and d in the figure refers to r values of 3.1, 2.6, 2.1, and 1.7, respectively. They were measured *in situ* in a three electrode Swagelok cell where the current is imposed between the two electrode materials. The electrolyte is EC + DEE (50:50) + 1M LiClO_4 .

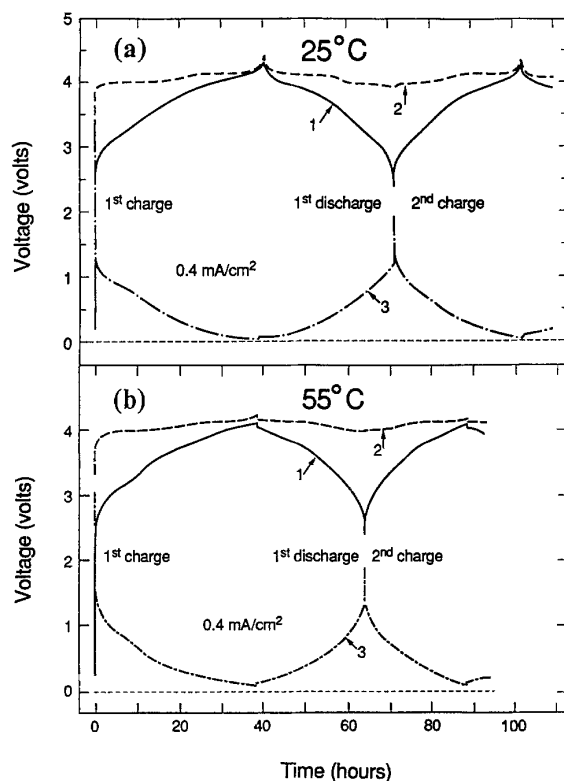


Fig. 12. The first cycles at a current of 0.4 mA/cm² of LiMn₂O₄/carbon (petroleum coke) cells in EC + DEE (50:50) + 1M LiClO₄ electrolyte, cycled at 25°C between 4.35 and 2.3 V and at 55°C between 4.1 and 2.3 V are shown in (a) and (b), respectively. The curves denoted by 1 represent the output voltage of the cells while the dashed curves denoted by 2 and 3 represent the voltage of the LiMn₂O₄ and carbon electrode, respectively, vs. lithium used as the third reference electrode. They were measured *in situ* in a three electrode Swagelok cell where the current is imposed between the two electrode materials.

and the negative electrode is completely lithiated with the composition Li_{0.5}C₆ at a voltage close to 0.02 V vs. Li.

Cycling behavior.—Figure 12 shows the first cycles at room temperature of a LiMn₂O₄/carbon battery operating at room temperature and the voltage profiles vs. Li of each electrode separately as obtained with the three electrode Swagelok cell. The open-circuit voltage before the first cycle is very close to 0 V (generally between -0.1 and +0.2 V), and the cell can be short-circuited without any capacity change before the first use, which is an advantage for this type of cell. At the first charge, under constant current, the cell voltage reaches about 2 V immediately with negligible capacity. This corresponds to the carbon voltage drop from its open-circuit voltage (close to 3.3 V vs. Li) to the voltage where the reduction reaction begins (close to 1.2 V vs. Li), as seen previously. The first charge takes longer than the first discharge; this means that all the capacity is not recovered. This irreversible loss at first half cycle was observed during the cycling behavior on both electrodes vs. Li (Fig. 3 and Fig. 6). After the first charge, on subsequent cycles, the system is reversible, as shown by the equivalent time of the charge and discharge; the Li⁺ ions are then rocked reversibly back and forth between the two intercalation compounds. The end of the first discharge to 2.4 V occurs when all the Li⁺ ions have been removed from the carbon, while the LiMn₂O₄ is not fully lithiated back, as seen by the respective voltages of both electrode vs. Li (Fig. 12a). This observation simply results from the intrinsic electrochemical behavior of each electrode material vs. lithium, and, more precisely, from the largest relative capacity loss of the carbon than the

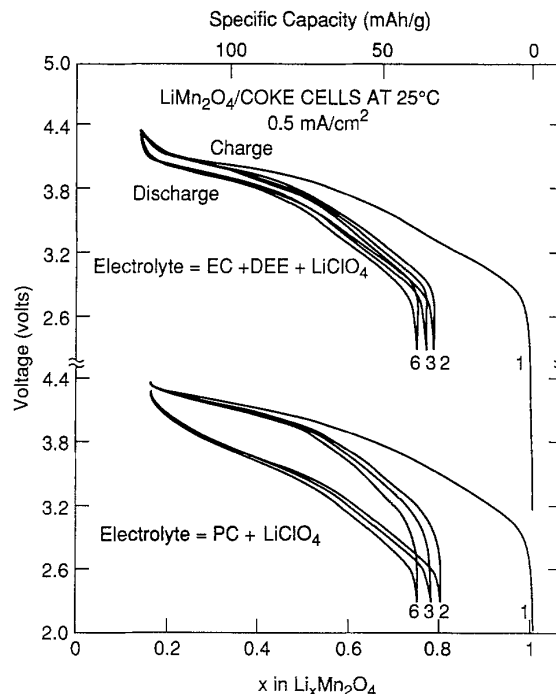


Fig. 13. Cycling behavior at a current rate of 0.5 mA/cm² of LiMn₂O₄/carbon rocking-chair cells at 25°C between 2.3 and 4.35 V in EC + DEE (50:50) + 1M LiClO₄ and PC + 1M LiClO₄ electrolytes. $r = 2.1$. $m_+ = 63$ mg and $m_- = 30$ mg. Thicknesses: $e_+ = 0.51$ mm and $e_- = 0.45$ mm.

LiMn₂O₄ electrode during the first cycle. Consequently, from these three electrode measurements, we learn that the mass ratio ($r = 2.1$) is well chosen to get fully deintercalated LiMn₂O₄ and fully intercalated carbon (with the composition Li_{0.5}C₆ at 0.02 V vs. Li) at the end of the first charge of the rocking-chair cell, and that the capacity of this cell is limited by carbon at the end of the first discharge and at the end of subsequent discharges.

The typical voltage-composition curves at room temperature of LiMn₂O₄/carbon optimized cell ($r = 2.1$) are shown on Fig. 13 for the few first cycles. The polarization is quite low, for instance, 0.13 V in EC-based electrolyte and remains almost constant over all the capacity range and over subsequent cycles. The variation of the specific capacity as a function of the discharge number is shown on Fig. 14. Note the high reversibility of the cell. A 5% loss appears during the 5 first charge/discharges and then during the next 15 charge/discharges, afterwards the cell maintains 90% of its original capacity.

The first cycles of the rocking-chair cell (with $r = 2.1$) and the voltage profiles of the two electrodes vs. Li at 55°C are shown on Fig. 12b. The charge voltage was limited to 4.1 V, a lower value than that used at room temperature. Figure 15 shows that the rocking-chair cell cycle well at 55°C with, however, a capacity loss after the first charge which is higher than at room temperature. The capacity as a function of the cycle number at 55°C is shown in Fig. 14 when the charge cut-off voltage was limited to 4.1 V. The curve follows the one obtained at room temperature in a parallel manner, but with a lower capacity. The use of a charge cut-off voltage lower than at room temperature is paid in terms of the available capacity and the data show that only 75% of the capacity is used at 55°C compared to room temperature if long cycle life is needed.

Influence of the current.—A rocking-chair battery is made with two intercalation compounds and intercalation reaction rates are usually low. So an important question is to know the current limit of these cells. A typical cell ($r = 2.1$, total active mass of electrodes = 93 mg) is cycled with constant charge current and increasing discharge current at

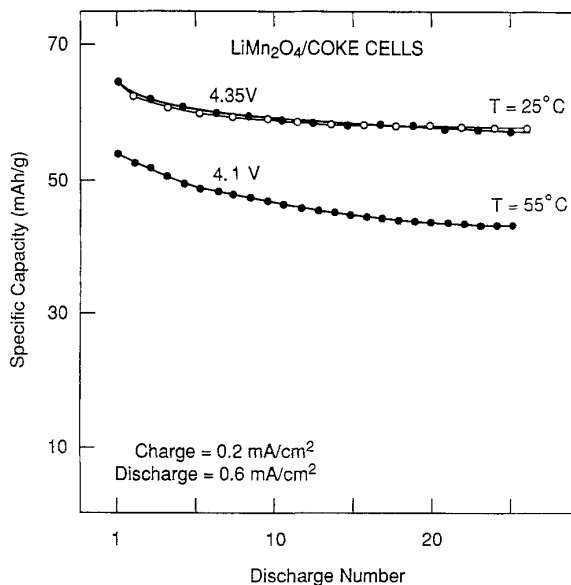


Fig. 14. Capacity vs. cycle number for LiMn_2O_4 /carbon (petroleum coke) cells as a function of the operating temperature, $T = 25$ and 55°C . The electrolyte is EC + DEE (50:50) + 1M LiClO_4 for the solid dot curves and PC + 1M LiClO_4 for the open dot curves. The charge and discharge current are, respectively, 0.2 mA/cm^2 and 0.6 mA/cm^2 and the discharge cut-off voltage is 2.3 V . Note that at 55°C the charge cut-off voltage has been lowered to preserve the reversibility of the cell (see text).

each cycle until the discharge capacity decreases by about a factor of three, and then is cycled with the initial discharge current. The result is shown on Fig. 16a. When the discharge current increases from 1 mA/cm^2 to 5 mA/cm^2 , the capacity at first stays almost constant and then de-

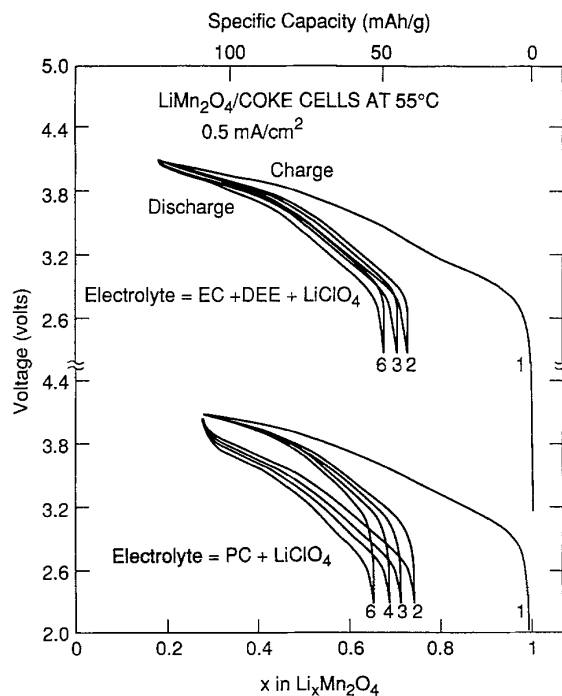


Fig. 15. Cycling behavior at a current of 0.5 mA/cm^2 of LiMn_2O_4 /carbon rocking-chair cells at 55°C between 2.3 and 4.1 V in EC + DEE (50:50) + 1M LiClO_4 and PC + 1M LiClO_4 electrolytes; $r = 2.1$, $m_+ = 21 \text{ mg}$, and $m_- = 10 \text{ mg}$. Thicknesses: $e_+ = 0.17 \text{ mm}$ and $e_- = 0.15 \text{ mm}$.

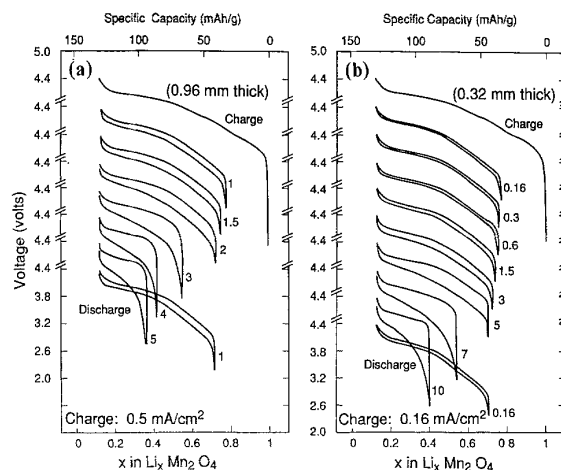


Fig. 16. Cycling behavior at 25°C of a LiMn_2O_4 /carbon rocking-chair cells between 2.2 and 4.35 V in EC + DEE (50:50) + 1M LiClO_4 as a function of electrode thicknesses using constant charging current but various discharge current. In (a) $r = 2.1$, $m_+ = 63 \text{ mg}$, and $m_- = 30 \text{ mg}$. Thicknesses: $e_+ = 0.51 \text{ mm}$ and $e_- = 0.45 \text{ mm}$. The charging current is 0.25 mA/cm^2 and successive increasing discharge currents of 1 mA/cm^2 , 1.5 mA/cm^2 , 2 mA/cm^2 , 3 mA/cm^2 , 4 mA/cm^2 , 5 mA/cm^2 , and then again 1 mA/cm^2 have been used; In (b), $r = 2.1$, $m_+ = 21 \text{ mg}$, and $m_- = 10 \text{ mg}$. Thicknesses: $e_+ = 0.17 \text{ mm}$ and $e_- = 0.15 \text{ mm}$. The charging current is 0.08 mA/cm^2 and increasing successive discharge currents of 0.16 mA/cm^2 , 0.3 mA/cm^2 , 0.6 mA/cm^2 , 1.5 mA/cm^2 , 3 mA/cm^2 , 5 mA/cm^2 , 7 mA/cm^2 , 10 mA/cm^2 , and then again 0.16 mA/cm^2 have been used.

creases dramatically above 2 mA/cm^2 , with increasing polarization. The normal capacity and polarization for a seventh cycle are then recovered when the initial low current rate is put back. This shows that the high current rate demand did not affect the reversibility of the cell. The same study has been made with thinner pellets, everything else being the same, and one can observe, as expected, that the current limit increases with decreasing pellet thickness. For instance, a cell made with pellets three times thinner can handle a current of 5 mA/cm^2 with negligible loss in capacity (Fig. 16b), and at a current as high as 10 mA/cm^2 the output capacity remains 27 mAh/g , i.e. barely less than $1/3$ of the initial capacity. Again, the normal capacity is recovered when a low current is used. The ability of these cells to sustain high currents is a function of the electrodes thickness as shown in Fig. 17. This quite usual observation results from a shortening in the Li^+ transport path through the pores of the pellets (i.e., a shorter time transfer for the Li^+ ions) as the thickness of the pellet decreases. These re-

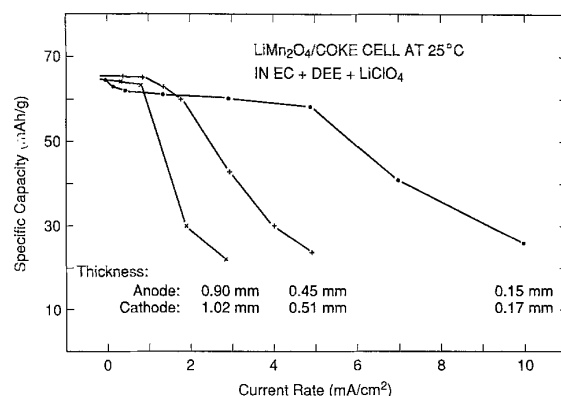


Fig. 17. Capacity vs. current for LiMn_2O_4 /carbon (petroleum coke) cells in EC + DEE (50:50) + 1M LiClO_4 electrolyte cycled at 25°C between 4.35 and 2.3 V and using electrodes of similar surface but different thicknesses.

sults show that this rechargeable rocking-chair battery system can handle high currents at room temperature if thin electrode technology is used.

Influence of an overcharge or an overdischarge.—We previously showed that the LiMn_2O_4 /carbon cells are carbon limited at the end of the first discharge to 2.4 V. This presents the advantage that, when the cell is discharged to 0 V, the voltage of the negative electrode (C vs. Li) increases reversibly to 3.9 V, but with negligible capacity (Fig. 6), so that the voltage of the positive electrode (LiMn_2O_4 vs. Li) remains almost constant. Thus, these rocking-chair batteries can be discharged safely to 0 V.

At the end of any charge, the positive electrode is $\lambda\text{-MnO}_2$ with a high voltage of about 4.3 to 4.4 V vs. Li and the negative electrode has the composition of $\text{Li}_{0.5}\text{C}_6$ with a low voltage close to 0.02 V vs. Li. If the cell is overcharged (applied voltage > 4.4 V), then the manganese oxide voltage vs. Li increases and the carbon voltage vs. Li decreases, so that either electrolyte oxidation decomposition, or Li plating (or both) are likely to occur.

Rocking-chair cells were made with electrode mass ratios different from 2.1, to study separately each situation. A ratio of 1.7 (i.e., a cell with an excess of carbon) was selected to study what happens when the electrolyte oxidation occurs on the positive electrode under normal operating conditions ($V \geq 0.02$ V vs. Li) of the negative electrode. At the end of the first charge the cell voltage reached a pseudo-plateau related to the electrolyte oxidation (Fig. 18), and on subsequent cycles the degradation of the cell occurs rapidly, a situation similar to that previously observed and discussed for $\text{LiMn}_2\text{O}_4/\text{Li}$ cells when overcharged above 4.5 V vs. Li. This kind of behavior has also been observed in LiCoO_2 /carbon cells when no caution is taken for the charge cut-off voltage (27).

Conversely, a cell with an excess of LiMn_2O_4 ($r = 3.5$) allowed for a study of the consequence of Li plating on the carbon without any decomposition of the electrolyte on the other electrode. Such a cell cycles well, with higher average output voltage than what is obtained with $r = 2.1$, but is not Li metal-free within our experimental conditions.

Storage properties.—We studied the self-discharge of a rocking-chair cell, with the optimized electrode mass ratio of 2.1 and using EC + DEE (50:50) + 1M LiClO_4 electrolyte, let under open circuit at 4.05 V after 2 charge-discharge cycles (Fig. 19). The measurement was done by monitoring the variation of the open-circuit voltage of the cell as a function of time and the capacity loss was deduced from the known open-circuit voltage vs. capacity variation of

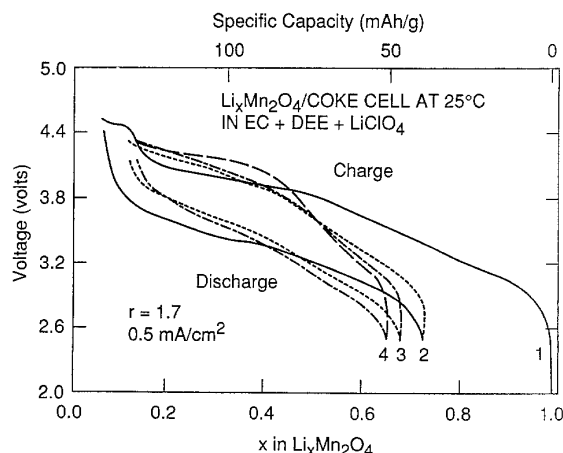


Fig. 18. Cycling behavior at a current of 0.5 mA/cm^2 of a LiMn_2O_4 /carbon rocking-chair cell made with an electrode mass ratio of 1.7, at 25°C in EC + DEE (50:50) + 1M LiClO_4 electrolyte. The cell was cycled till 4.5 V at the first charge and then only to 4.35 V. The discharge limit was 2.5 V. $m_+ = 51 \text{ mg}$ and $m_- = 30 \text{ mg}$.

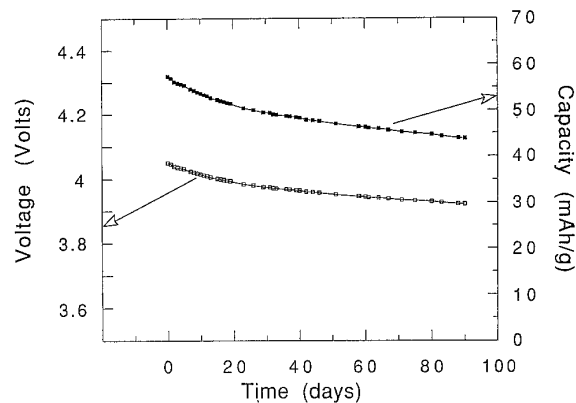


Fig. 19. Open-circuit voltage and calculated capacity of a LiMn_2O_4 /carbon rocking-chair cell (161 mg of active material) using EC + DEE (50:50) + 1M LiClO_4 as the electrolyte under self-discharge at room temperature. The self-discharge was measured after the cell had been cycled once in the whole voltage range (2.4 to 4.35 V) and then charged up to 4.1 V at a current rate of 0.35 mA/cm^2 .

this cell. The capacity loss (Fig. 19) first drops quickly and is not a linear function of time while after a few days the decrease in capacity becomes small and changes linearly with time. From the slope of the linear part of the curve one can deduce a loss rate. Thus, by extrapolation, one can estimate that the cell will lose about 40% of its initial capacity after six months, compared to the 30% capacity loss of the recently reported D-size Sony's rocking-chair cells (13) or the 60% loss of commercialized D-size Ni-Cd cells. After 2 months, an identical cell was cycled between 4.35 and 2.3 V and its behavior was similar to that of a freshly made cell, indicating that the capacity loss in open circuit can be recovered by recharging the cell. We are now investigating the self-discharge of these batteries after a charge to different voltage limits.

Power performances.—At room temperature and when cycled at low current rates the $\text{LiMn}_2\text{O}_4/\text{EC} + \text{DEE}$ (50:50) + 1M LiClO_4 /carbon cells with $r = 2.1$ deliver at first discharge a calculated specific capacity of 67 mAh/g of active electrode materials, an average output voltage of 3.7 V and a calculated specific energy of 250 Wh/kg of active electrode materials (Fig. 12). These values are reduced to 60 mAh/g , 140 mAh/cm^3 , 230 mWh/g , and 490 mWh/cm^3 , respectively, if the carbon black and the binder, which are mixed with the active materials, are taken into account. For comparison, a rocking-chair cell with $r = 2.6$ in which the carbon is intercalated to its composition limit $\text{Li}_{0.7}\text{C}_6$ has an output voltage of 3.75 V and deliver 65 mAh/g and 244 mWh/g of composite electrode materials. In practical hardware, because of packaging, one usually assumes a 33% realization of the experimental specific values based on active materials (28). The specific capacities of both LiMn_2O_4 /carbon and LiNiO_2 /carbon (19), estimated this way, are compared in Fig. 20 with those for commercially available Ni-Cd batteries and Sony's prototype Li^+ ion rechargeable batteries (13). Note that, under this assumption, LiMn_2O_4 /carbon cells have almost the same specific capacity as Ni-Cd. Furthermore, because of their larger output voltage (3.7 V compared to 1.2 V for Ni-Cd), their specific energy is about three times higher (85 mWh/g compared to 30 mWh/g for Ni-Cd).

In order to evaluate the power rate of LiMn_2O_4 /carbon cells and compare it with that of lead-acid and Ni-Cd batteries, the so-called Ragone plot, is shown in Fig. 21. Again a 33% realization factor has been assumed on the experimental specific values (both energy and power) based on active materials. The interesting feature is that the curve for the LiMn_2O_4 /carbon cells, using the lower electrode thickness, is parallel to that of Ni-Cd indicating that this cell can deliver high output power similar to Ni-Cd batteries, with a specific energy remaining three times higher. When using thicker electrode pellets, the output power is

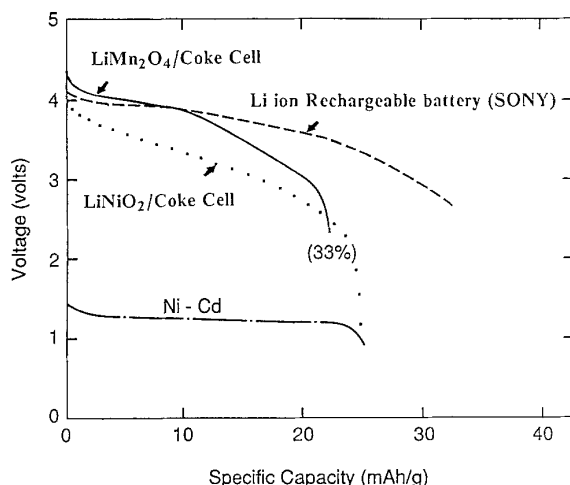


Fig. 20. Extrapolation of the discharge behavior of $\text{LiMn}_2\text{O}_4/\text{carbon}$ (petroleum coke) cells in $\text{EC} + \text{DEE}$ (50:50) + 1M LiClO_4 and of $\text{LiNiO}_2/\text{carbon}$ cells to practical hardware with a hypothetical realization factor of 33% (see text), as compared to the discharge behavior of commercialized D-size nickel-cadmium batteries (13) and of the D-size Li ion rechargeable batteries $\text{LiCoO}_2/\text{carbon}$ announced by Sony Energtec (13).

limited by an important factor, due to the importance of Li^+ transport phenomena (as discussed previously). If thin or thick film technology is used, for instance, to build spiral cells (e.g. of AA, C, or D size), higher current rates, and thereby higher specific powers, could be achieved.

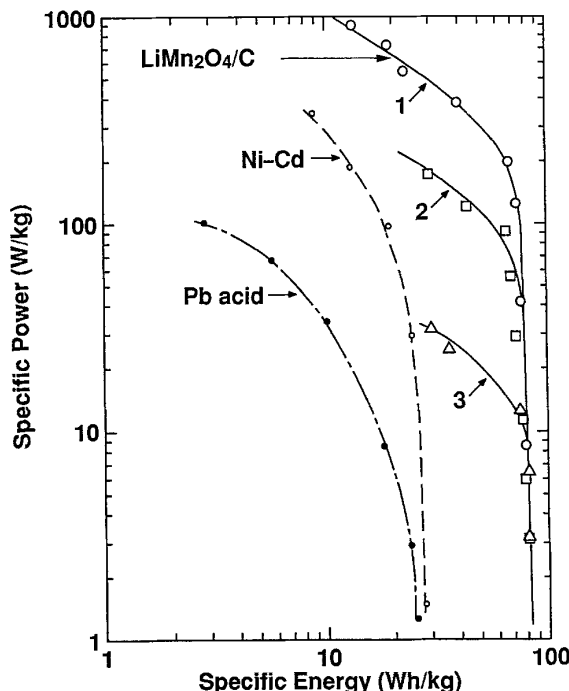


Fig. 21. Ragone plots of $\text{LiMn}_2\text{O}_4/\text{carbon}$ (petroleum) cells of three different thicknesses of the composite electrodes, in $\text{EC} + \text{DEE}$ (50:50) + 1M LiClO_4 electrolyte, extrapolated to practice hardware with a hypothetical realization factor of 33%, as compared to presently commercialized secondary lead acid (portable sealed battery of 61.7 cm^3) and D-size (55 cm^3) nickel-cadmium cells (13). The pellet thicknesses used for the $\text{LiMn}_2\text{O}_4/\text{carbon}$ cells are the following. 1: $e_+ = 0.085\text{ mm}$ and $e_- = 0.08\text{ mm}$. 2: $e_+ = 0.17\text{ mm}$ and $e_- = 0.15\text{ mm}$, 3: $e_+ = 0.51\text{ mm}$ and $e_- = 0.45\text{ mm}$.

Conclusions

In this study we optimized the behavior of rechargeable rocking-chair secondary cells based on LiMn_2O_4 positive electrodes and carbon negative electrodes, and we showed that they operate safely at room temperature and at 55°C (when the charge cut-off voltage is drastically controlled), exhibit good cycling behavior, can be discharged down to 0 V and, in addition, can sustain high currents if thin electrodes are used. The two electrolytes $\text{PC} + 1\text{M LiClO}_4$ and $\text{EC} + \text{DEE}$ (50:50) + 1M LiClO_4 have been shown to be compatible with the two electrode materials. We found that $\text{PC} + 1\text{M LiClO}_4$ allows a larger operating electrochemical window than $\text{EC} + \text{DEE}$ (50:50) + 1M LiClO_4 for LiMn_2O_4 at high voltage. However, we have shown that $\text{EC} + \text{DEE}$ (50:50) + 1M LiClO_4 can be used safely in the rocking-chair cells, even at high operating temperature (55°C). This solvent mixture enhances the electrolyte conductivity, thereby reducing the polarization of the rocking-chair cells and allowing a larger output voltage.

Preliminary measurements have indicated that the self-discharge of $\text{LiMn}_2\text{O}_4/\text{carbon}$ cells is relatively large. Lower self-discharges have been reported for other carbon rocking-chair systems in D size and coin cells using LiCoO_2 or LiNiO_2 as the positive electrode, respectively, instead of LiMn_2O_4 . Since the range of operating potential for cells using $\text{LiCoO}_2/\text{carbon}$ is similar to the $\text{LiMn}_2\text{O}_4/\text{carbon}$ cells, it is possible that the larger self-discharge measured in our system could be due to different cell design and/or different constructive hardware used for our measurements. However, coin cells have been made using stainless steel 1225 coin cell hardware (12 mm diam and 2.5 mm thickness) obtained from Rayovac Corp. These cells use pellets of 109 mg (of active material) LiMn_2O_4 and 52 mg (active material) carbon, corresponding to a specific capacity and a specific energy of 10.8 mAh and 40 mWh, respectively. The experiments done so far indicate that all the cycling results obtained with these coin cells are nearly identical to those obtained using Swagelok cells. We are presently investigating the self-discharge (a relevant parameter) of these coin cells to test the assumption about cell design and hardware.

Finally, to fully use the total capacity of both electrodes in order to maximize the specific capacity and specific energy of these rocking-chair cells, we are now studying the behavior of carbon rocking-chair cells using $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ as the starting material (i.e., using the excess x of Li content as a Li reservoir to compensate for the large irreversible loss at the carbon electrode at first cycle) and the results of such a study will be described in a forthcoming paper (29). The use of a LiClO_4 -based electrolyte is not the most attractive choice for the commercial use of these batteries. The search for substitute candidates is being addressed.

Acknowledgments

We would like to thank J. H. Wernick, W. R. McKinnon, F. K. Shokoohi, P. Warren, G. Baker, and S. Colson for helpful discussions and J. Gural for the technological constructions needed in this work. We also thank Sid Meghead of Rayovac Corporation for supplying the coin cell hardware and Conoco Inc. for the petroleum coke.

Manuscript submitted July 16, 1991; revised manuscript received Nov. 9, 1991.

Bellcore assisted in meeting the publication costs of this article.

REFERENCES

1. D. P. Wilkinson, J. R. Dahn, U. Von Sacken, and D. T. Fouchard, Abstracts 53 and 54, p. 85 and 87, The Electrochemical Society Extended Abstracts, Vol. 90-2, Seattle, WA, October 14-19 (1990).
2. D. W. Murphy, F. J. DiSalvo, J. N. Carides, and J. V. Waszczak, *Mat. Res. Bull.*, **13**, 1395 (1978).
3. D. W. Murphy and J. N. Carides, *This Journal*, **126**, 349 (1979).
4. M. Lazzari and B. Scrosati, *ibid.*, **127**, 773 (1980).

5. M. Armand, in "Materials for Advanced Batteries," D. W. Murphy, J. Broadhead, and B. C. H. Steele, p. 145, Plenum Press, New York (1980).
6. K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough, *Mat. Res. Bull.*, **15**, 783 (1980).
7. J. J. Auborn and Y. L. Barbario, *This Journal*, **134**, 638 (1987).
8. J. M. Tarascon, *ibid.*, **132**, 2089 (1985).
9. R. Kanno, Y. Takeda, T. Ichikawa, K. Nakanishi, and O. Yamamoto, *J. Power Sources*, **26**, 535 (1989).
10. M. Mohri, N. Yanagisawa, Y. Tajima, H. Tanaka, T. Mitate, S. Nakajima, M. Yoshida, Y. Yoshimoto, T. Suzuki, and H. Wada, *ibid.*, **26**, 545 (1989).
11. J. R. Dahn, R. Fong, and M. J. Spoon, *Phys. Rev. B*, **42**, 6424 (1990).
12. J. R. Dahn, U. Von Stacken, and R. Fong, Abstract 42, p. 66, The Electrochemical Society Extended Abstracts, Vol. 90-2, Seattle, WA, October 14-19 (1990).
13. T. Nagaura, 4th International Rechargeable Battery Seminar, Deerfield Beach, Florida (1990).
14. Y. Nishi, H. Azuma, and A. Omaru, U.S. Pat. 4,959,281 (1990).
15. J. M. Tarascon and D. Guyomard, *This Journal*, **138**, 2864 (1991).
16. S. A. Campbell, C. Bowes, and R. S. McMillan, *J. Electroanal. Chem.*, **284**, 195 (1990).
17. J. M. Tarascon, E. Wang, F. K. Shokoohi, W. R. McKinnon, and S. Colson, *This Journal*, **138**, 2859 (1991).
18. R. Fong, U. Von Sacken, and J. R. Dahn, *ibid.*, **137**, 2009 (1990).
19. J. R. Dahn, U. Von Sacken, M. W. Juskow, and H. Al-Jabany, *ibid.*, **138**, 2207 (1991).
20. J. T. Dudley, D. P. Wilkinson, G. Thomas, R. LeVae, S. Woo, H. Blom, C. Horvas, M. W. Juskow, B. Denis, P. Juric, P. Aghakian, and J. R. Dahn, *J. Power Sources*, **35**, 59 (1991).
21. W. Weppner and R. A. Huggins, *Ann. Rev. Mater. Sci.*, **8**, 269 (1978).
22. C. J. Wen, B. A. Boukamp, R. A. Huggins, and W. Weppner, *This Journal*, **126**, 2258 (1979).
23. M. M. Thackeray, P. J. Johnson, L. A. de Picciotto, P. G. Bruce, and J. B. Goodenough, *Mat. Res. Bull.*, **19**, 179 (1984).
24. M. H. Rossouw, A. de Kock, L. A. de Picciotto, M. M. Thackeray, W. I. F. David, and R. M. Ibberson, *ibid.*, **25**, 173 (1990).
25. T. Ohzuku, M. Kitagawa, and T. Hirai, *This Journal*, **137**, 769 (1990).
26. M. M. Thackeray, W. I. F. David, P. G. Bruce, and J. B. Goodenough, *Mat. Res. Bull.*, **18**, 461 (1983).
27. R. S. McMillan, Abstract 43, p. 68, The Electrochemical Society Extended Abstracts, Vol. 90-2, Seattle, WA, October 14-19 (1990).
28. E. Plichta, M. Salomon, S. Slane, M. Uchiyama, D. Chua, W. B. Ebner, and H. W. Lin, *J. Power Sources*, **21**, 25 (1987).
29. J. M. Tarascon and D. Guyomard, To be published by *This Journal*.

The Electrochemical Reduction of 2-Ethyl Anthraquinone

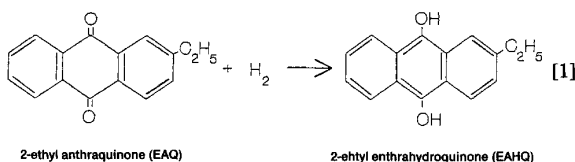
R. F. Knarr,* M. Velasco, S. Lynn,* and C. W. Tobias**

Department of Chemical Engineering, University of California, Berkeley, California 94720

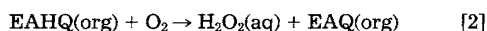
ABSTRACT

The electrochemical reduction of 2-ethyl anthraquinone (EAQ), an alternate step in the production of hydrogen peroxide, is shown to be feasible in a two-phase system consisting of a mixture of ethyl benzene and tributyl phosphate, and aqueous sodium hydroxide. The initial reduction product on the most effective cathode material, lead, is the sodium salt of the hydroquinone (Na_2EAHQ). In this system the reactant, EAQ, has very low solubility in the aqueous phase whereas the product, Na_2EAHQ , is similarly insoluble in the organic phase. The results of this investigation may be of interest to the study of other systems with these solubility characteristics. Electrolysis was carried out under well-defined conditions of vigorous turbulence in a cell in which a rotating cylindrical cathode was separated from the cylindrical anode by a coaxial Nafion membrane. At a rotational rate of 2000 rpm, about equal volumes of the organic and aqueous phases could be suspended in the cell while keeping the aqueous phase continuous. Current-voltage behavior was mass-transfer limited and hence was a function of rate of rotation, organic/aqueous phase ratio, and EAQ concentration in the organic phase. The maximum cathodic limiting current density achieved was 30 mA/cm^2 . Current efficiencies approached 100% for the reduction of EAQ when operating at 50% of the limiting current. The electrochemical reaction was shown to take place at the three-phase boundary: organic/aqueous/lead. A flow-through porous-electrode cell, using lead-plated, reticulated vitreous carbon for the cathode, was constructed to promote more intimate contact between the reactant and the electrode. The maximum current density for EAQ reduction achieved in this cell was 177 mA/cm^2 based on the projected cathode area.

2-Ethyl anthraquinone (EAQ) is used in the large-scale manufacture of hydrogen peroxide (1). In this process EAQ, dissolved in a solvent (or mixture of solvents), is first reduced to 2-ethyl anthrahydroquinone (EAHQ)

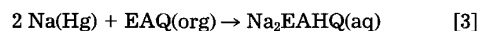


The hydroquinone solution is then contacted with oxygen. A spontaneous reaction forms product hydrogen peroxide and the quinone, which is recycled



Lynn and Paalman (2) developed an EAQ-based process for making hydrogen peroxide using sodium amalgam as the reducing agent. This process involves production of an intermediate, the disodium salt of 2-ethyl anthrahydroquinone (Na_2EAHQ), with subsequent acidification to yield the autoxidizable hydroquinone.

The initial step to give the disodium salt is the reaction of amalgamated sodium with 2-ethyl anthraquinone



This step involves the intimate contact of three separate liquid phases: mercuric, organic, and aqueous. The metallic sodium is soluble only in the mercury, the EAQ is soluble only in the organic solvent, and the intermediate disodium salt of the hydroquinone is soluble only in basic aqueous solution. If the aqueous phase were not present, the salt would precipitate on the mercury and cause the reaction to slow and, rather quickly, to terminate.

The final step in this process, the formation of EAHQ, is the neutralization of the disodium salt with an acid

* Electrochemical Society Active Member.

** Electrochemical Society Fellow.