

THE $\text{Li}_{1-x}\text{Mn}_2\text{O}_4/\text{C}$ ROCKING-CHAIR SYSTEM: A REVIEW

J. M. TARASCON and D. GUYOMARD

Bellcore, Red Bank, NJ 07701, U.S.A.

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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 $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ 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 cycling behavior. However, in rocking chair cells a price is paid in terms of average

Li-ion battery

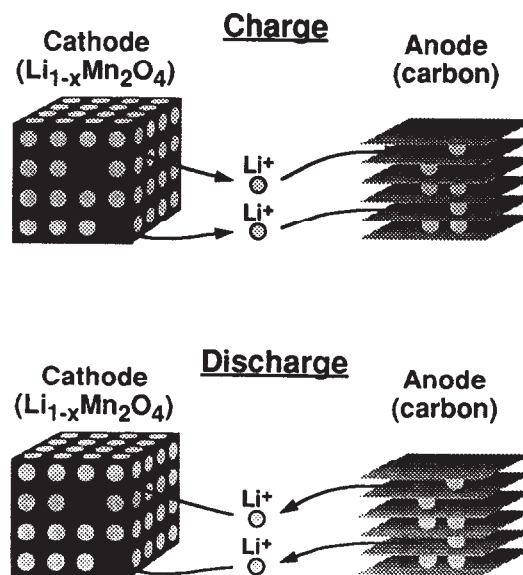


Fig. 1. The charge and discharge mechanism for a Li-ion battery is shown (both the cathode and anode materials are intercalation compounds).

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 Energtec[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 $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ spinel phase as the positive electrode and a form of carbon as the negative electrode[18–20].

Our $\text{LiMn}_2\text{O}_4/\text{C}$ 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

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 $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ 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 $\text{Li}_{1+x}\text{Mn}_2\text{O}_4/\text{Li}$ 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 ($<600^\circ\text{C}$) via a sol gel route that consists in using LiOH and Mn acetates as precursors[27] leading to small particle sizes ($<2\mu\text{m}$). 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 ethylene propylene diene monomer (EPDM) in a solution of cyclohexane, or polyvinylidene fluoride (PVDF) in a solution of cyclopentanone, 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 Swagelok 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 either 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

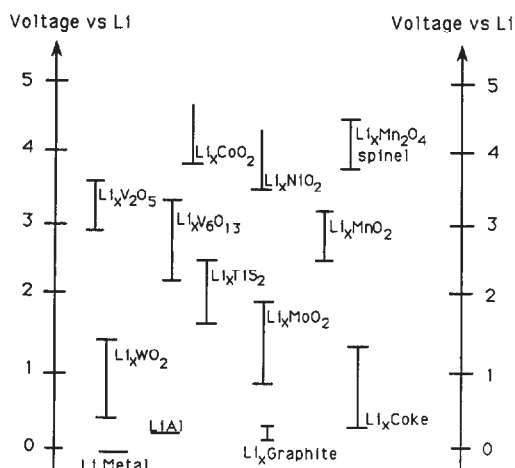


Fig. 2. Electrochemical potential range of Li intercalation (as measured with respect to Li metal) for a wide variety of compounds are shown.

amount of intercalated species x in $\text{Li}_x\text{Mn}_2\text{O}_4$ 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 ($10\text{--}50\text{ mV h}^{-1}$).

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 $\text{LiMn}_2\text{O}_4/\text{LiClO}_4$ 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 ($\text{Li}_{0.55}\text{C}_6$) (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 $\text{LiMn}_2\text{O}_4/\text{Electrolyte}/\text{Li}$ electrochemical cell to 4.3 V vs. Li results in a $\lambda\text{-MnO}_2$ phase. This phase was reported to be metastable and to decompose upon heating in air into a non Li-intercalable $\beta\text{-MnO}_2$ 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 $\beta\text{-MnO}_2$, but rather an evolution of the λ -phase to the ε and then finally to the $\beta\text{-MnO}_2$ phase. Finally, powders left at 55°C for three months were still pure $\lambda\text{-MnO}_2$, 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

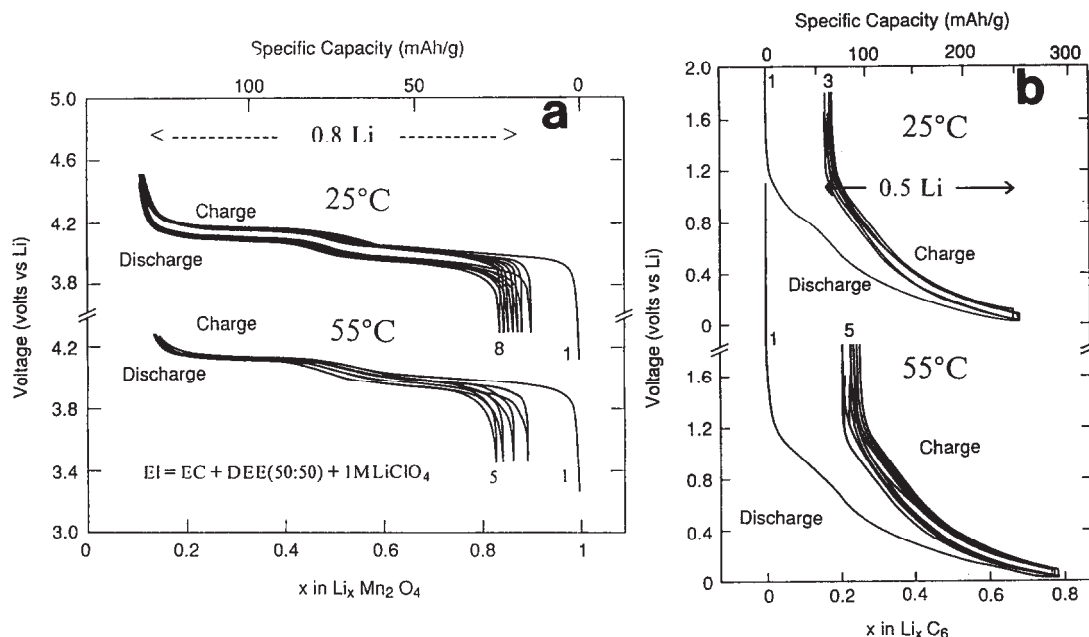


Fig. 3. The typical cycling behavior at 25 and 55°C for a $\text{LiMn}_2\text{O}_4/\text{EC} + \text{DEE}(50:50) + 1\text{ M LiClO}_4/\text{Li}$ (a) and a C (petroleum coke)/ $\text{EC} + \text{DEE}(50:50) + 1\text{ M LiClO}_4/\text{Li}$ (b) is shown. The spinel-based cell was cycled at a C/10 rate in contrast to C/20 for the carbon-based cell. EC = ethylene carbonate, DEE = diethoxyethane.

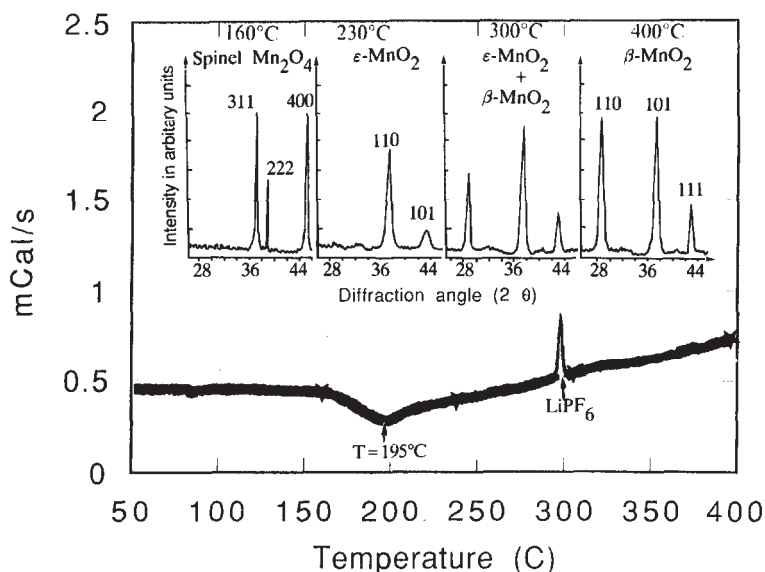


Fig. 4. Differential scanning calorimetric measurements (DSC) for a delithiated LiMn_2O_4 (ie $\lambda\text{-MnO}_2$) sample (see text). The phase transformation occurs at 195°C . The inset shows the X-rays taken at position marked by asterisks on the DSC curve. The ambient was air and the temperature 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 Swagelok 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 $\text{LiMn}_2\text{O}_4/\text{LiClO}_4$ 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 $\text{LiMn}_2\text{O}_4/\text{Electrolyte}/\text{Li}$ has an open circuit voltage of 3.5 V). A reaction may occur

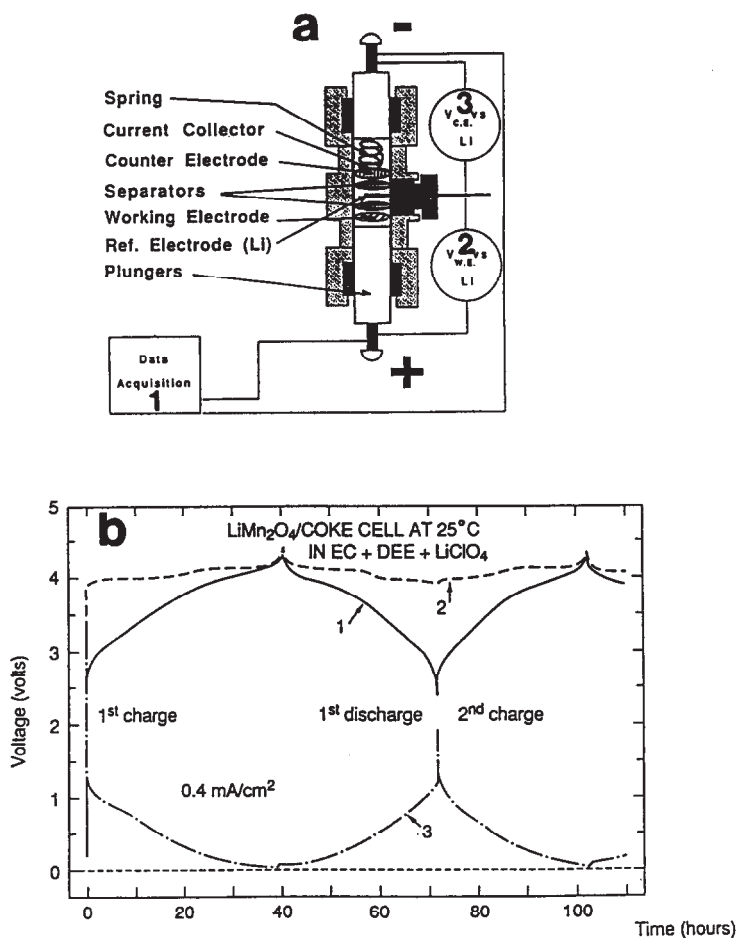


Fig. 5. The schematic of a three-electrode cell is shown in (a) and the first cycles at room temperature of a $\text{LiMn}_2\text{O}_4/\text{EC} + \text{DEE}(50:50) + 1 \text{ M LiClO}_4/\text{C}$ (petroleum coke) three-electrode cell, under constant current, are shown in (b). The voltage measured at 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.

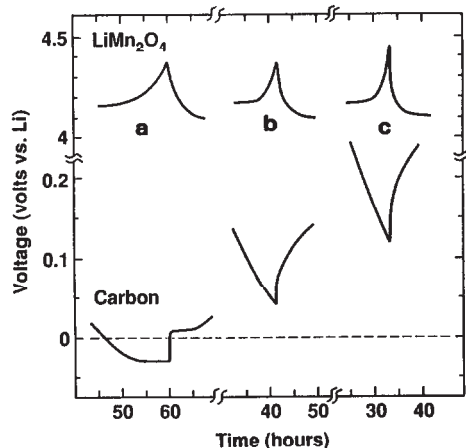


Fig. 6. Voltage profiles vs. Li (as measured from a three electrode cell) of LiMn_2O_4 and carbon electrodes at the end of the first charge and the beginning of the first discharge with different ratios $r = 3.1$ (a), $r = 2.1$ (b) and $r = 1.7$ (c). For these experiments the mass of the carbon electrode was maintained constant (30 mg), the electrolyte used was $\text{EC} + \text{DEE} (50:50) + 1 \text{ M LiClO}_4$ 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.

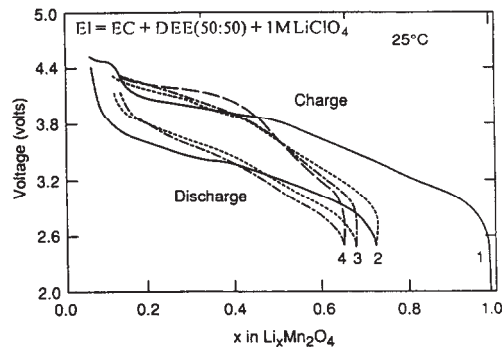


Fig. 7. The cycling behavior of a cell using a weight ratio (positive to negative electrode) of 1.7 (51/30 mg) is shown. The cell was cycled at 0.5 mA cm^{-2} between 0 and 4.5 V during the first charge and then between 2.5 and 4.35 on subsequent cycles.

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