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High voltage stable liquid electrolytes for $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /carbon rocking-chair lithium batteries

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Abstract

A high voltage oxidation-resistant electrolyte is required for $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /carbon rocking-chair cells that need to be charged up to a voltage higher than 4.3 V. Many electrolyte compositions have been tested for their ability to resist to high voltages on $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ electrodes and their ability to maintain high ionic conductivity in a wide temperature range. This survey allowed us to select new electrolyte compositions in the system dimethyl carbonate (DMC)+ethylene carbonate (EC)+lithium hexafluorophosphate (LiPF_6) that are kinetically stable up to almost 5 V versus lithium at 55 °C on $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ electrodes. Low rate potentiostatic experiments, coupled with coulombmetric measurements in the 4.25–5.1 V range, allowed to select the following compositions: (DMC+EC) (1:2)+1 M LiPF_6 and (DMC+EC) (2:1)+1.5 M LiPF_6 as the best. These compositions have been used in practical $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /carbon rocking-chair batteries and show better performance in terms of cycle life and self-discharge over a wider temperature range. They are compatible with rocking-chair batteries based on LiCoO_2 and LiNiO_2 as well.

Keywords: Rocking-chair lithium batteries; Electrolytes; Rechargeable lithium batteries

1. Introduction

An inherently safe approach to lithium batteries is to replace lithium metal with a lithium intercalation compound, leading to the so-called ‘rocking-chair lithium’ or ‘lithium-ion’ rechargeable batteries. Interest for this technology has increased ever since the announcement in 1990 by Sony Energytec Inc. [1] and Moli Energy Ltd. [2] that this approach could be realized when a carbon compound is used for the negative electrode, and a highly oxidizing lithium metal oxide (LiCoO_2 and LiNiO_2 , respectively) for the positive electrode. The Bellcore rocking-chair battery, proposed a few months later [3,4], is based on the spinel $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ as the positive electrode and either coke or graphite as the negative electrode.

The various carbon-based rocking-chair lithium batteries have comparable performances, are environmentally safe, possess higher specific energies and energy densities than competitive technologies (Ni–Cd and Ni–metal hydride), exhibit good rate capability and long cycle life. The rocking-chair lithium technology is very promising for the consumer electronics market, where the needs for personal portable electronics (such as

electric tools, appliances, etc.) and in communications are becoming greater. The Sony battery was commercialized in June 1991 and several other battery companies (Sanyo, Matsushita, Hitachi, Yuasa) are now developing the lithium-ion technology using a liquid non-aqueous Li^+ -conducting organic electrolyte. AA-size cylindrical prototypes of batteries based on the Bellcore system have been built in 1992.

The output voltage of a rocking-chair lithium cell, determined by the difference between the electrochemical potential of lithium within the two lithium intercalation electrodes, is large in order to produce substantial energy values. Carbon negative electrodes operate in a very reducing voltage range (<1.2 V versus lithium) at which most electrolytes are thermodynamically reduced, and the deposition of an efficient passivating layer at the carbon surface during the first cycle is necessary to get further reversible behavior. The lithium metal oxide positive electrode must be charged up to more than 4 V versus lithium more than 4.1 V for LiCoO_2 [1] and LiNiO_2 [2], and more than 4.3 V for $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ [5]), at which electrolyte oxidation may occur. Electrolyte oxidation leads to irreversible losses in capacity because of the generation of chemical species, which deposit as an insulating layer on the electrode surface or evolve as a gas, thus increasing

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the internal pressure in the cell. Electrolyte oxidation is believed to be the main failure mechanism for rocking-chair technology.

For the above reasons, minimizing electrolyte oxidation is a major requirement in enhancing the cycle life and improving the high-temperature performance of the actual rocking-chair lithium batteries. Most of the electrolyte combinations can be used beyond the voltage range of their thermodynamic stability because the electrolyte oxidation reaction is kinetically limited. However, owing to the important influence of non-predictible catalytic activity of the electrode surface towards electrolyte oxidation, the search for new electrolyte compositions is quite empirical and various electrolyte compositions have to be tested systematically.

In this paper, studies allowing for the selection of good electrolyte compositions for $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /carbon rocking-chair batteries are detailed with emphasis on low scan-rate potentiostatic experiments in the 4.25–5.1 V range versus lithium. Experiments performed in order to understand the behavior of the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /electrolyte interface at high voltage and the self-discharge mechanism of a complete rocking-chair cell are reported. Finally, cycling data, obtained on laboratory test cells and AA-size research prototypes using the best electrolyte composition, are presented.

2. Experimental

The experimental conditions, including materials synthesis, preparation of composite electrodes and a description of swagelock laboratory cells, have been described in detail elsewhere [5]. In the present study, poly(vinylidene difluoride) (PVDF) binder was mixed with $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ and carbon black (Super S from Ensagri Corporation), with a (5:85:10) mass ratio, to prepare the positive composite electrode. Aluminum substrates, with a surface area of 1 cm^2 were used as the current collectors for the positive electrodes. All the solvents tested in this work have been purified and dried by double distillation and the salts have been vacuum dried, according to conventional procedures. Battery testings were performed by means of a 'Mac-Pile' system using a two-electrode configuration. The ionic conductivity of different electrolyte compositions was measured over a wide temperature range (from -25 to $65\text{ }^\circ\text{C}$) using a conventional conductivity cell with the help of a high frequency impedance analyser. The melting points were determined using a differential scanning calorimeter while the boiling points were measured at equilibrium using a reflux system.

3. Results

3.1. Selection of the best electrolyte compositions

The most important figures-of-merit of an 'ideal' electrolyte for a carbon-based rocking-chair lithium battery are the following:

(i) the electrolyte oxidation rate, which has to be as low as possible on the positive electrode up to $55\text{ }^\circ\text{C}$ for voltages higher than 4.3 V versus lithium;

(ii) the use of a perchlorate-free salt, for safety reasons;

(iii) the ionic conductivity, which has to be as high as possible in order to lower the electrode polarization and the internal resistance of the cell;

(iv) the melting and boiling points, which have to be as low as possible and as high as possible, respectively, in order to allow for a wide operating temperature range, and

(v) the complete compatibility of the electrolyte with the carbon negative electrode down to 0 V versus lithium.

3.1.1. Rapid screening

Usually when the material/electrolyte/Li cell is continuously charged under constant current (a typical rate is $C/5$) up to very high voltage (we choose 5.1 V), the electrolyte oxidation voltage on that material can be taken as the voltage at which an unlimited capacity is obtained. The irreversibility of this plateau is checked by further discharging the cell. In practice, an unlimited voltage plateau is not always observed experimentally, in which case the electrolyte oxidation voltage has been taken as the voltage at which an extra irreversible capacity of 20 to 30% of the reversible intercalation capacity is obtained. This technique is very convenient for a rapid screening of many different electrolyte compositions to get a first selection of several compositions that may be interesting to look at more carefully.

The results of several tests performed on $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /(DEE + EC)(1:1) + 1 M salt/Li cells are summarized in Table 1. For the same solvent composition that we selected for our earlier studies and the same composite positive electrode material ($\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ + carbon black + organic binder (85:10:5 by mass)), the common lithium salts can be classified according to their ability to give an oxidation-resistant electrolyte. Because $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ breakdown voltage was lowered upon cycling, LiClO_4 is then the only salt that could be used, with this solvent mixture, to operate the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ -based rocking-chair batteries, that justifies our previous choice [5].

Keeping the perchlorate salt, different solvent mixtures have then been tested. Because DMC-based electrolytes gave excellent results, a given composition of DMC + EC has been kept and the salt been changed,

Table 1

Voltage breakdown of the electrolyte compositions: (EC + DEE)(1:1) + 1 M salt, measured on a $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ composite electrode ($\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ + 10% carbon black) using a galvanostatic mode (see text), as a function of the type of salt

Salt	LiClO_4	$\text{LiN}(\text{CF}_3\text{SO}_2)_2$	LiCF_3SO_3	LiAsF_6	LiPF_6	LiBF_4
Breakdown voltage vs. Li (V)	4.55	4.4	4.1	3.9	3.8	3.4

keeping in mind that the wanted electrolyte needs to be perchlorate-free because of safety reasons. The results are presented in Table 2, which shows that within the same solvent composition ((DMC + EC)(1:1)) and the same composite positive electrode material ($\text{Li}_{1+x}\text{Mn}_2\text{O}_4$), the usual lithium salts can be classified for their resistance to oxidation, in the following way: $\text{LiClO}_4 \approx \text{LiPF}_6 \approx \text{LiBF}_4 > \text{LiAsF}_6 > \text{LiN}(\text{CF}_3\text{SO}_2)_2 > \text{LiCF}_3\text{SO}_3$. This second classification shows that the resistance degree to oxidation of an electrolyte does depend on both the solvents constituents and the type of salt, leading to the impossibility of defining a general rule how to select the best electrolyte, even for a given composite electrode material. Consequently, two salts, LiPF_6 and LiBF_4 , could be used. However, LiBF_4 is not as good because of its lower ionic conductivity.

We further focussed on electrolytes made with LiPF_6 salt and the mixture of carbonate-based solvents, and we fixed the salt concentration (to 1 M), while varying the solvent or the solvent mixture. Pure EC-based electrolyte was not studied because of its too high freezing point (close to 0 °C), not compatible with practical application. Results show that among the investigated solvent mixtures, most of the usual carbonate-based solvents could be used with the exception of pure DEC. However, pure DMC-based electrolyte is not compatible with carbon negative electrodes, at which no passivation layer builds up upon cycling, while the presence of PC cosolvent is not compatible with graphite negative electrode.

Mixtures of the three components, DMC, EC and LiPF_6 , were then studied further to check if they are acceptable in terms of melting and boiling points, and ionic conductivity.

The influence of the solvent composition and the salt concentration on the melting and boiling points of (DMC + EC + LiPF_6)-based electrolytes has been examined. Results show that the range of composition (DMC + EC)(3:7) to (8:2) + (1 M to 2 M) LiPF_6 corresponds to melting and boiling points with perfectly

acceptable values in the range from –20 to –23 °C and from 105 to 130 °C, respectively. Increasing amounts of EC cosolvent lead to an increase of the boiling point while increasing the salt concentration leads to a decrease of the melting point.

Measurement of the ionic conductivity of (DMC + EC + LiPF_6)-based electrolytes at room temperature showed that maximal values of 10 to 11 mS/cm are obtained in the range of composition (DMC + EC)(3:7) to (8:2) + (1 M to 2 M) LiPF_6 . These values are among the highest that can be obtained when using various lithium salts in the DMC + EC mixture.

At this stage of our investigations, the range: (DMC + EC)(3:7) to (8:2) + (1 M to 2 M) LiPF_6 was found to correspond to very good electrolyte compositions, as they are oxidation resistant on the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ composite positive electrode, perfectly acceptable in terms of width of liquid temperature range and ionic conductivity, and compatible with carbon-negative electrodes, both coke and graphite. Note that if only compatibility of the electrolyte with coke is required, and not with graphite, then the four-component mixtures DMC + EC + PC + LiPF_6 could be used.

3.1.2. Fine selection

To refine further the best electrolyte composition, another technique allowing for accurate and reproducible quantitative measurement of electrolyte oxidation, is needed. Low scan-rate potentiostatic experiments coupled with coulombmetric measurements have been used for such a purpose.

A potentiostatic study of the same $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ material with the (DMC + EC)(1:2) + 1 M LiPF_6 electrolyte, compared with a classical (DEE + EC)(1:1) + 1 M LiClO_4 electrolyte, shows (see Fig. 1) that the electrolyte electroactivity range is increased by more than 0.7 V [6], even at 55 °C which represents extremely difficult conditions. When the voltage is cycled in the 4.2–5.1 V range, the current remains low and stabilizes after

Table 2

Voltage breakdown of the electrolyte compositions: (EC + DMC)(1:1) + 1 M salt, measured on a $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ composite electrode ($\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ + 10% carbon black) using a galvanostatic mode (see text), as a function of the type of salt

Salt	LiClO_4	LiPF_6	LiBF_4	LiAsF_6	$\text{LiN}(\text{CF}_3\text{SO}_2)_2$	LiCF_3SO_3
Breakdown voltage vs. Li (V)	> 5.1	> 5.1	> 5.1	4.7	4.35	3.2

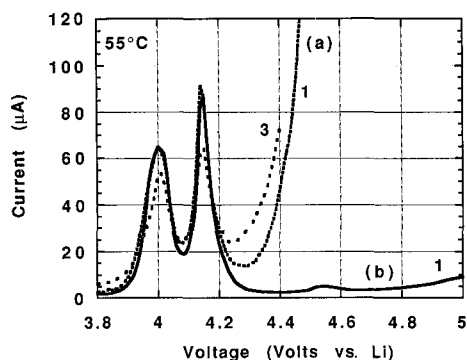


Fig. 1. Voltammograms of an $\text{Li}_{1+x}\text{Mn}_2\text{O}_4/\text{Li}$ cell at 55 °C using: curve (a) (EC+DEE)(1:1)+1 M LiClO_4 electrolyte, (1) during the first charge and (3) during the third charge, and curve (b) the new electrolyte composition (DMC+EC)(1:2)+1 M LiPF_6 ; scan rate=10 mV/h, and mass of the active material=10 mg.

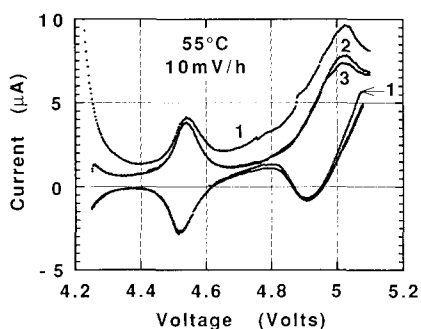


Fig. 2. Cyclic voltammograms in the high voltage range of an $\text{Li}_{1+x}\text{Mn}_2\text{O}_4/\text{Li}$ cell at 55 °C using the new electrolyte composition (DMC+EC)(1:2)+1 M LiPF_6 ; the three first cycles are shown; scan rate=10 mV/h, and active material mass=10 mg.

two cycles, as shown in Fig. 2. This behavior can be interpreted in terms of a mixture of two reversible processes, characterized by the two sets of reversible peaks at 4.55 and 4.95 V versus lithium, and an irreversible process, characterized by the background current, corresponding to electrolyte oxidation. The reversible processes have been studied elsewhere [7].

The extra capacity due to electrolyte oxidation can be calculated over the voltage ranges where the reversible processes are complete (4.4–4.7 V and 4.7–5.1 V) from half the algebraic sum of the total measured capacities during the anodic and cathodic scans (Q^+ and Q^- , respectively), assuming the complete reversibility of the intercalation processes:

$$Q_i = (Q^+ + Q^-)/2 \quad (1)$$

The values thus obtained for second cycle are then scaled per 0.1 V ($q_i = Q_i/\Delta V$ with $\Delta V = 0.3$ and 0.4 in the ranges 4.4–4.7 V and 4.7–5.1 V, respectively) and the results are reported as q_i/Q_r in terms of percentage of irreversible capacities per 0.1 V, q_i , per usable capacity, Q_r (in the 3.5–4.4 V range).

Several carbonate-based solvents mixed with various lithium salts were tested [8]. The DMC+EC+ LiPF_6

system showed better results than the DEC+EC+ LiPF_6 one. Selected results obtained within the DMC-based system are shown in Tables 3 and 4. Even with these difficult test conditions (high temperature, high voltage, low scan rate [6]), extremely low values of excess electrolyte oxidation capacities were measured, thus demonstrating quantitatively the exceptional stability of these electrolyte compositions on $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ electrodes. A larger cycle life and a lower self-discharge are expected by further minimizing the electrolyte oxidation irreversible capacity. Results show that, keeping 1 M concentration of LiPF_6 , the best solvent composition corresponds to 33% of DMC, while for a fixed DMC+EC composition of 2:1, a 1.5 M salt concentration is preferred. Consequently the electrolyte compositions (DMC+EC)(1:2)+1 M LiPF_6 and (DMC+EC)-(2:1)+1.5 M LiPF_6 appear to be the best for $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ composite electrode. Moreover, they are completely compatible with carbon-negative electrodes, both petroleum coke and graphite [9]. Their main characteristics are summarized in Table 5.

The selected electrolyte compositions are also compatible with LiNiO_2 and LiCoO_2 materials. Results show that voltages as high as 5 V versus lithium can be achieved as well, with low irreversible capacity loss due to electrolyte oxidation, the major problem being then the intrinsic unstability of Li_xMO_2 ($M = \text{Co}, \text{Ni}$) materials for $x < 0.5$.

Table 3

Irreversible capacity per 0.1 V to normal reversible capacity ratio (see text) measured at 55 °C after second cycle on a $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ composite electrode ($\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ +10% carbon black), as a function of the DMC content y of the (DMC+EC+1 M LiPF_6) electrolyte. The $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ -active mass was 10 mg and the scan rate was 40 mV/h

DMC content y	0.33	0.5	0.67
q_i/Q_r in 4.4–4.7 V (%)	0.33	0.40	0.53
q_i/Q_r in 4.7–5.1 V (%)	1.5	2.0	2.7

Table 4

Irreversible capacity per 0.1 V to normal reversible capacity ratio (see text) measured at 55 °C after second cycle on a $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ composite electrode ($\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ +10% carbon black), as a function of the LiPF_6 concentration of the ((DMC+EC)(2:1)+: LiPF_6) electrolyte. The $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ active mass was 10 mg and the scan rate was 40 mV/h

xM LiPF_6	0.5	1	1.5	2
q_i/Q_r in 4.4–4.7 V (%)	2.3	0.53	0.33	0.50
q_i/Q_r in 4.7–5.1 V (%)	5.5	2.7	1.0	2.0

Table 5
Summary of the characteristics of the new electrolyte compositions

Electrolyte composition	(DMC+EC)(1:2)+1 M LiPF ₆	(DMC+EC)(2:1)+1.5 M LiPF ₆
Melting point (°C)	-20	-23
Boiling point (°C)	130	105
Conductivity at room temperature (mS/cm)	11	10.5
Conductivity at 0 °C (mS/cm)	5	4
Conductivity at -20 °C (mS/cm)	1.2	0.8
Safe oxidation, at room temperature	4.9 V vs. Li	4.9 V vs. Li
Limit vs. Li, at 55 °C	4.8 V vs. Li	4.8 V vs. Li

3.2. Understanding the high voltage behavior

Various experiments have been performed in order to understand the phenomena occurring in the 4.2–5.1 V range [6]. In this section we will try to understand how the different components of the positive composite electrode contribute to the electrolyte oxidation.

The voltammograms obtained with Al/electrolyte/Li and Al/binder/electrolyte/Li cells (Fig. 3, curve (1)) show no current up to 5.1 V versus lithium, indicating that there is no measurable electrolyte oxidation on the aluminum surface and no oxidative degradation of the binder, in this voltage range. The voltammogram obtained with carbon black/electrolyte/Li cell after two cycles (Fig. 3, curve (2)) is compared with that of the complete Li_{1+x}Mn₂O₄ composite/electrolyte/Li cell (Fig. 3, curve (3)) in the same conditions. The current is very close to the background current obtained on the composite electrode, demonstrating that the electrolyte oxidation measured on Li_{1+x}Mn₂O₄ composite occurs mainly at the surface of carbon black. To get more quantitative information, we varied the amount of carbon black mixed with the active material and measured the electrolyte oxidation irreversible capacities, as described in the previous section. The main result is a linear dependence of the electrolyte oxidation capacity

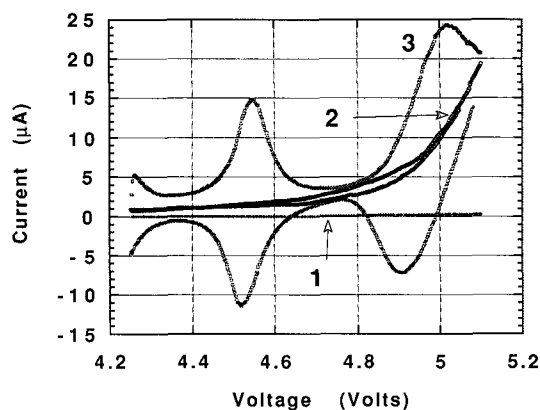


Fig. 3. Cycling voltammograms during the third cycle of different cells at 55 °C: curve (1) Al/electrolyte/Li and Al/binder/electrolyte/Li cells; curve (2) carbon black/electrolyte/Li cell, and curve (3) Li_{1+x}Mn₂O₄ composite/electrolyte/Li cell.

on the total surface area of the composite, including active material and carbon black surface areas. The much larger carbon black surface area compared with that of the active material (by a factor close to 75) explains why electrolyte oxidation seems to occur mainly on carbon black in electrodes using a standard black amount (10% by mass).

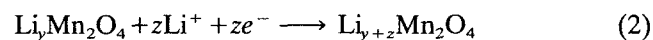
As a result, the carbon black content was reduced to 3% (in mass) in our composite positive electrodes, which gives a good compromise between low electrolyte oxidation at high voltage and a cycling rate fast enough (C/2) allowing for maximal experimental capacity [6].

It is worth noting that any increase in the active material specific area leads to an increase of the electrolyte oxidation irreversible capacity in the high voltage range. Consequently, a compromise between high cycling rates (favored by small particle size and high surface area) and low electrolyte oxidation extra capacities needs to be found.

3.3. Self-discharge mechanism of Li_{1+x}Mn₂O₄/coke rocking-chair cells

As a first step, the self-discharge of the positive half-cell Li_{1+x}Mn₂O₄ composite/electrolyte/Li was investigated.

The variation of the open-circuit voltage of such a cell with time at room temperature is reported in Fig. 4(a), after a charge-up to 4.8 V. This curve looks like a usual discharge curve (voltage versus capacity) with a first voltage plateau at 4.53 V and a second one at 4.2 V. That is the reason why we calculated the inverse of the derivative of this curve and plotted it as a function of voltage, see Fig. 4(b), curve (1). The discharge voltammogram for pure Li_{1+x}Mn₂O₄, calculated by subtracting the current measured on pure carbon black from the total current measured on the composite, is plotted in the same graph (curve (2)) for comparison. The excellent correlation between both curves demonstrates that the self-discharge at Li_{1+x}Mn₂O₄ electrode corresponds to a lithium intercalation within the LiMn₂O₄ structure, according to the reaction:



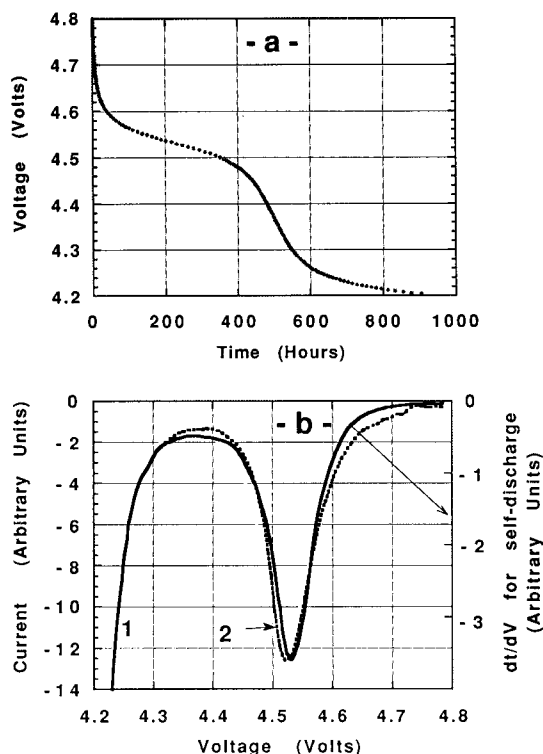
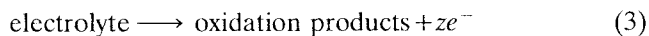


Fig. 4. (a) Open-circuit voltage of an $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ composite/electrolyte/Li cell at room temperature after a charge-up to 4.8 V. (b) dt/dV vs. voltage calculated variation is compared with the calculated voltammogram for pure $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ (see text).

where electrons are coming from electrolyte oxidation, occurring in this high voltage range, according to:



The self-discharge mechanism at a positive composite electrode charged above 4.2 V and kept under open-circuit is then a local redox process involving the two previous half-reactions.

As a second step, the self-discharge of a complete coke-based rocking-chair cell was studied with the help of a three-electrode cell [6].

The variation of $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ and coke voltages versus lithium and of the rocking-chair output voltage, were recorded simultaneously under open circuit (Fig. 5) in the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4/\text{Li}/\text{coke}$ three-electrode cell after charging the cell up to 4.5 V. The decay of the output voltage with time is due to both the decay of $\text{Li}_{1+x}\text{Mn}_2\text{O}_4/\text{Li}$ voltage and the increase of coke/Li voltage. The decay of $\text{Li}_{1+x}\text{Mn}_2\text{O}_4/\text{Li}$ voltage is due to the local redox process evidenced previously. The increase of the coke/Li voltage corresponds to a lithium de-intercalation from lithiated coke.

This latter reaction could be explained by a local redox process as well, involving the two following half-reactions:

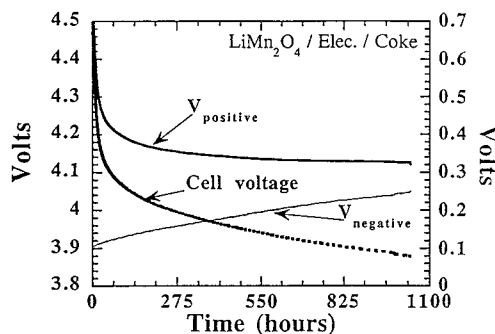
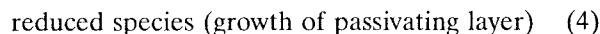
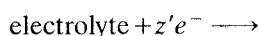


Fig. 5. Open-circuit output voltage of a coke-based rocking-chair cell and open-circuit voltage of both electrodes vs. Li measured in the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ composite/Li/coke three-electrode cell after a charge-up to 4.5 V at room temperature.

and:



where the second reaction is thermodynamically possible due to the very reducing potential (a few hundreds of mV) but is kinetically slow due to the already existing passivating layer on the coke surface. In this case of the existence of totally independent processes at the electrodes, the amount of lithium intercalated or de-intercalated in the positive or negative, respectively, should be independent, leading to the imbalance of the cell. Cycling the coke-based cell after 1000 h of self-discharge gave a reversible capacity with the same order of magnitude (about 5% less) as the capacity before self-discharge, indicating that the two processes taking place at the electrodes are not independent.

To explain this experimental result, one may consider that some oxidated species generated at the positive electrode could diffuse or migrate to the negative electrode to be reduced or the parallel mechanism for reduced species generated at the negative electrode. In this case, no capacity loss should be recorded after a self-discharge experiment. A partial capacity loss might be explained by the presence of both the local processes and redox shuttle.

More systematic experiments are then necessary to elucidate the mechanism of self-discharge in a complete rocking-chair battery.

3.4. Behavior of $\text{Li}_{1+x}\text{Mn}_2\text{O}_4/\text{coke}$ rocking-chair cells

$\text{Li}_{1+x}\text{Mn}_2\text{O}_4/\text{coke}$ rocking-chair cells using the new electrolyte compositions, cycled at $C/2$ in the 2-4.7 V range, show excellent cycle life, owing to the high oxidation stability of the new electrolyte compositions. Laboratory test cells have reached more than 2500 cycles at room temperature and more than 500 cycles at 55 °C with a capacity close to 60% of the initial one [10].

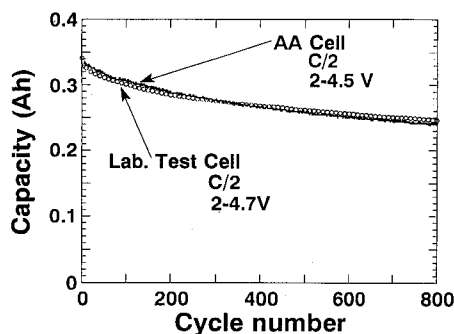


Fig. 6. Comparison of the capacity variation upon cycling between 2 and 4.5 V at C/2 of a coke-based rocking-chair laboratory test cell and an AA-size research prototype.

AA-size cylindrical prototypes using $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /electrolyte/coke system have been built in the Moli pilot plant in Vancouver, Canada. Various tests show that all the results obtained using laboratory test cells can be extrapolated to the AA-size, see Fig. 6.

4. Conclusions

We have proposed a convenient technique to screen various electrolyte compositions that lead to the selection of the best mixture for $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /carbon cells. A rapid screening, taking into account the stability against oxidation on $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, the ionic conductivity, the liquid temperature range and the compatibility with both coke and graphite, allowed us to narrow the range of electrolyte compositions that are worth for further careful investigation: mixtures of EC+DMC+LiPF₆ were selected. The fine selection of the best compositions was performed with the help of slow scan-rate voltammetry coupled with very precise coulombmetric measurements in the high voltage range at high temperature (55 °C).

The optimum compositions are (DMC+EC)(3:7 to 8:2)+(1 M to 2 M) LiPF₆ with the best behavior

obtained for the (DMC+EC)(1:2)+1 M LiPF₆ and (DMC+EC)(2:1)+1.5 M LiPF₆ mixtures. These electrolyte compositions can be used at voltages up to 4.9 V at room temperature and 4.8 V at 55 °C. Moreover, they are liquid in the temperature range from -20 °C to more than 105 °C, and exhibit excellent ionic conductivity between -20 and 65 °C, making them attractive for practical cells.

The effective stability of these electrolytes against oxidation is the key of better performance, mainly large reversible capacity, long cycle life and low self-discharge, of practical $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ /carbon cells in a wider temperature range.

Finally, the selected electrolyte compositions are also compatible with LiCoO₂ and LiNiO₂ materials. This type of electrolyte opens a completely new research field on the study of materials that are electrochemically active in the 4-5 V range versus lithium.

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