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Short communication

# Lithium intercalation cells $LiMn_2O_4/LiTi_2O_4$ without metallic lithium

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**Abstract**

Rechargeable lithium cells can be made with two different intercalation compounds as the positive and negative electrodes, which are safer than the battery technology using pure Li metal. In this paper, we present our study of the Li ion type battery that uses $LiTi_2O_4$ as the negative electrode, which is coupled with a strongly oxidizing intercalation compound, spinel $LiMn_2O_4$, as the positive electrode has been found to solve problems associated with the use of metallic lithium at the expense of lowering the overall cell voltage. Preliminary electrochemical data revealed that this Li ion type battery "$LiMn_2O_4/LiTi_2O_4$" exhibits a low performance in terms of capacity. Li cycling efficiency is examined with mixed solvents as electrolyte. With improvements in capacity, materials such as these could improve the over all performance of secondary lithium intercalation cells.



*Keywords:* Electrolyte; Intercalation cell; Rocking chair

## 1. Introduction

Over the last two decades, research on rechargeable lithium batteries (a battery that uses Li metal as the negative electrode) has been rapidly promoted. This is due to the high specific capacity, 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 high energy densities much larger than other systems. Research on transition-metal oxides suitable as hosts for rapid insertion/extraction of ions has led to the development of $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ as cathode materials in rechargeable lithium battery [1]. However, development of secondary lithium cells using an intercalation compound as the positive electrode and Li as the negative have been slow due to their operation and safety limitations associated with the use of Li metal [2–5]. In addition, because of poor cycling efficiency, three-to four-fold excess lithium metal must be present in practical cells, leading to irreversible chemical and structural changes in the cathode [6]. This excess lithium increases the equivalent volume of the negative electrode by the multiplication factor and therefore, reduces the energy density for the lithium cell. To solve this problem, one approach is to replace the lithium metal negative electrode with a lithium alloy or compound, such as LiAl [7], $LiFe_2O_3$ or $LiC_6$ [8,9]. Although these materials stabilize the lithium, this reduces the energy density of the cell, since the added material is not used in the operation of the system. Even with this drawback, several lithium batteries have been developed using this strategy. Rechargeable batteries for electric-vehicle applications require a long cycle life. For this to be possible, the electrochemical reactions must be highly reversible. Some of the most reversible electrodes operate through insertion reactions. So, it was realized that replacing the lithium metal with a lithium intercalation compound was a possible solution to high reactivity and irreversibilities of the solid lithium negative electrode; these are the so-called rocking chair batteries in which Li ions rock back and forth between the intercalation compounds during the electrochemical process [10]. In the rocking chair cell (hereafter called lithium ion cell), no lithium metal is necessary in this cell, and lithium is always held as a host in one of the electrodes.

Based on this, we propose to replace metallic lithium with a Li insertion metal oxide electrode in order to resolve major issues that limit the use of metallic lithium at the expense of lowering the overall cell voltage [11]; thus, oxidizing compounds are used as the positive electrode. There are three classes of Li-based compounds, based on $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ that satisfy this requirement. Among the three Li-based compounds the use of $LiMn_2O_4$ material offers the following advantages: (1) a lower overall electrode cost because of easier synthesis and the use of Mn which is

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naturally more abundant and cheaper than Co or Ni; (2) low toxicity; and (3) intercalation of a second lithium atom at an average voltage of 3 V, which improves the overall specific capacity of the batteries. Hence in this study, we used lithium ion batteries that employ the $LiMn_2O_4$ spinel phase as the positive electrode and the $LiTi_2O_4$ spinel phase as the negative electrode. The average plateau voltage for Li/$LiTi_2O_4$, i.e. the position of the redox voltage for titanium $Ti^{4+}/Ti^{3+}$ is 1.33 V [12], and because of its very low redox potential, we used this as an alternative material to lithium metal. The output voltage of such a cell is high as determined by the difference between the electrochemical potentials of Li within the two electrodes.

These Li ion batteries do not require a special manufacturing environment because intercalation compounds $LiMn_2O_4/LiTi_2O_4$ are not moisture sensitive and can be handled under ambient condition. The Li ion cell is assembled in its discharged state, when the output voltage is close to zero. The electrochemical behavior of lithium ion batteries has been studied with mixed solvents as electrolytes. Lithium cycling efficiency has been found to increase more for the electrolyte $LiClO_4$: PC–THF (PC: propylene carbonate; THF: tetrahydrofuran) than for the $LiClO_4$: EC–PC (EC: ethylene carbonate) electrolyte.

The objective of this work is to elucidate the possibility of using a reducing intercalation compound such as $LiTi_2O_4$ as a replacement for metallic lithium in secondary Li cells. Herein, we report the use of $LiTi_2O_4$, lithium titanium oxide, as a negative electrode and $LiMn_2O_4$, lithium manganese oxide, as a positive electrode material, and discuss the results. Along with this study, we also determine the lithium cycling behavior in EC–PC mixed electrolytes and compare it with that in PC–THF mixed electrolytes.

## 2. Experimental

### 2.1. Synthesis

$LiMn_2O_4$ powder was prepared by reacting a stoichiometric mixture of lithium carbonate, $Li_2CO_3$ (99.9% Soekawa Chemicals) and manganese III oxide, $Mn_2O_3$ (99.9% high purity chemicals) in a molar ratio of 1:2. They were mixed in ethanol and calcined at 700 °C for 10 h in air. The powder was then annealed at 850 °C for 24 h in air and slowly cooled to room temperature.

$LiTi_2O_4$ powder was prepared by reacting stoichiometric amounts of $Li_2CO_3$ (99.9% Soekawa Chemicals), $TiO_2$ (99.9% Soekawa chemicals) and $Ti_2O_3$(99.9% Kodan Kagaku). The constituents were combined and fired in a two-step process according to the over all reaction scheme

$$Li_2CO_3 + 2TiO_2 + Ti_2O_3 \rightarrow 2LiTi_2O_4 + CO_2 \quad (1)$$

After mixing in ethanol, the air stable components were fired at 750 °C in air for 2.5 h. The requisite amount of $Ti_2O_3$ was then mixed with the prefired material and pelletized. The pellets were sealed in evacuated quartz tubes for final firing at 850 °C for 18 h then, allowed to furnace cool to ambient temperature. Phase identification and evaluation of the lattice parameters of the product were carried out by powder X-ray diffraction (XRD) using Cu Kα radiation.

### 2.2. Electrochemical characterization

The procedures for the fabrication and the measurement of lithium rechargeable cells are almost the same as those described elsewhere [13]. The electrode active materials (spinel powder) were mixed with 15 wt.% of acetylene black [14] and with 10 wt.% of PVDF, and then pressed (wt.%: weight percent). The mixture was ground and then pressed into a disk with a diameter of 10 mm at 78 MPa. The thickness of each disk was 1 mm and the weight was about 60 mg. Each disk was dried at 80 °C for 30 min. Electrochemical performance was evaluated with cylindrical test cells made of stainless steel of 10 mm diameter. An electrochemical testing cell was constructed with the $LiMn_2O_4$ disk as the cathode, $LiTi_2O_4$ as the anode, and filter paper that was soaked in electrolyte as the separator. To ensure physical contact between cell components, a stainless steel spring that allowed a pressure of about 1 kg/cm$^2$ was connected outside the cell. The electrolyte used was 1 M $LiClO_4$ in EC–PC, 3:1 vol. and 1.25 M $LiClO_4$ in PC–THF 2:3 vol. (Tomiyama Chemicals). Cell performance was evaluated galvanostatically at a current density of 0.1 mA/cm$^2$ with the aid of charge–discharge equipment (Hokuto Denko HJ-201B). The cells were first charged and then discharged at constant current density between the potential limit of 0 V for discharge and 2.4 V for charge. Cell voltage was measured using a digital multimeter (Hioki 3223). These instruments were controlled through an IEEE 488 interfaced to a computer, which controlled the cycling experiments, and data were collected. It is important to note that all electrochemical measurements were carried out under ambient condition.

In general, propylene carbonate, because of its low vapor pressure is used as the solvent. To increase the ionic conductivity of the electrolyte without changing the nature and content of the Li salt, mixtures of solvents are generally used. Tobishima and Yamaji [15,16] examined the electrolytic characteristics of PC-high dielectric solvent mixed electrolytes. The high dielectric solvent, ethylene carbonate was used. EC has many desirable properties as an electrolyte solvent for lithium batteries, compared with PC. For example, EC has a high dielectric constant and lower viscosity than PC. These characteristics seem support the ionic dissociation of the solute and easy ion migration. Pistoia reported [17,18] high conductivity and a discharge capacity increase in $CuF_2$/Li with $LiClO_4$–EC electrolyte. But $LiClO_4$–EC alone as the electrolyte has a shortcoming in practical use its high melting point (36.2 °C). This can be overcome by mixing it with another solvent. Therefore, the electrochemical results (i.e. the charge–discharge behavior)

were evaluated with $LiClO_4$ in an EC–PC mixed solvent and the results were compared with that obtained using PC–THF mixed electrolytes.

## 3. Results and discussion

The X-ray diffraction patterns of $LiMn_2O_4$ and $LiTi_2O_4$ prepared by solid state reaction are shown in Figs. 1 and 2, respectively. The lattice parameter of the compound matched with those of the spinel structure powder diffraction file. $LiMn_2O_4$ was a single phase compound and the data for $LiTi_2O_4$ showed that the sample has a $Li_2Ti_3O_7$ as an impurity. Unless the preparation temperature is optimized, impurity phases are always formed. $LiMn_2O_4$ a strongly oxidizing compound, is a promising electrode reversibly de-intercalate lithium up to 4.5 V. The delithiation of this compound was, however, not characterized beyond 4.5 V since the electrolyte might be oxidized. The electrochemical charge and discharge curves for $LiMn_2O_4$ with respect to metallic lithium as anode, in our study, show that lithium atom can be extracted at a closed-circuit voltage of 4.3 V and the same amount can be reversibly inserted back into the structure on discharge. Hence, the process is electrochemically reversible, without any significant loss of capacity.

Lithium intercalated material, $LiTi_2O_4$, as the anode, shows sufficient reducing potential, making it a good match with the strongly oxidizing compound. The electrochemical characterization of spinel $LiTi_2O_4$, in our study, shows an average reversible potential of 1.5 V relative to metallic lithium. Due to its low voltage, we selected $LiTi_2O_4$ as a substitute for lithium metal at the expense of a lower voltage. The electrochemical properties of $LiMn_2O_4$ and $LiTi_2O_4$ versus Li metal well understood.

As we expected, intercalation cells that are made without any metallic lithium exhibit intermediate voltage related to the difference between positive ($LiMn_2O_4$: 4.3 V) and negative electrode ($LiTi_2O_4$: 1.5 V) potentials. The charge and discharge profiles for the $LiMn_2O_4/LiTi_2O_4$ intercalation cell at room temperature in ambient atmosphere are shown in Fig. 3. The electrochemical charge and discharge curves for $LiMn_2O_4/LiTi_2O_4$ at a current density of 0.1 mA/cm$^2$ in EC–PC electrolyte show that, during charge, Li is de-intercalated from $Li_{1-x}Mn_2O_4$ and is inserted into $Li_{1+x}Ti_2O_4$ at an average voltage of 2.3 V corresponding to 8 mAh/g (Fig. 3). During discharge, Li is intercalated into $Li_{1+x}Mn_2O_4$, and the length of the plateau at 2.3 V in the charge curve seen in Fig. 3 is programming shortened with in the discharge curve. The shape of the charge curve is characterized by an immediate sharp increase in voltage till 1.5 V followed by a gradual increasing sloping potential profile till the cut-off voltage of 2.4 V. Upon discharge, the cell voltage drops with a gradual downward sloping potential till 1.9 V and then sharply decreases to 0 V. Unlike metallic lithium, rocking chairs have no excess of Li in the anode or cathode, so they are tolerant of repeated discharge to 0 V. Current density is limited to low rates (0.05–0.1 mA/cm$^2$) while testing, and reducing the current restores the capacity (not shown here). This indicates that the loss of capacity may be a diffusion-limited phenomenon associated with the insertion process. $LiMn_2O_4/LiTi_2O_4$ intercalation cells (charge and discharge cycle) show an initial capacity of 14 mAh/g that decreases to 6 mAh/g after

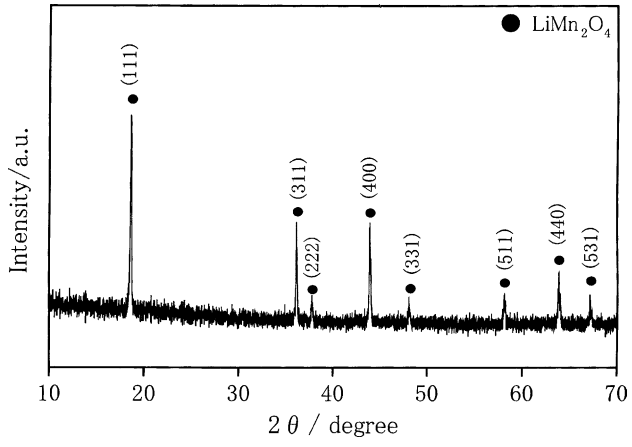


Fig. 1. X-ray diffraction pattern of $LiMn_2O_4$.

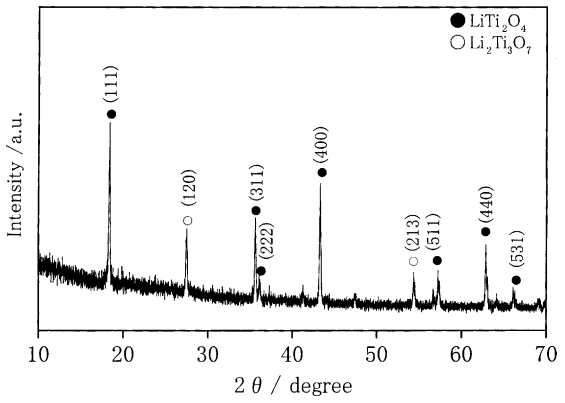


Fig. 2. X-ray diffraction pattern of $LiTi_2O_4$.

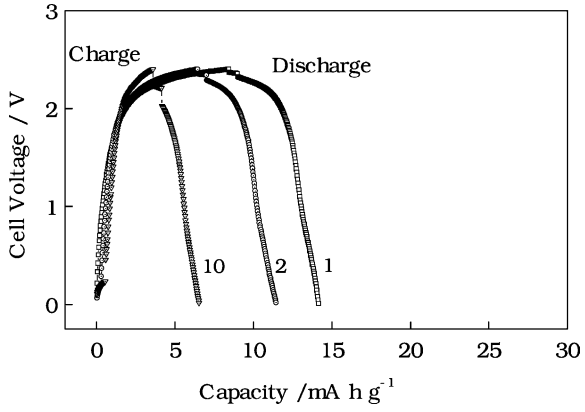


Fig. 3. Charge–discharge curve for the $LiMn_2O_4/LiTi_2O_4$ cell cycled at 0.1 mA/cm$^2$ in EC–PC electrolyte for various cycles. Cycle numbers are indicated in the figure.

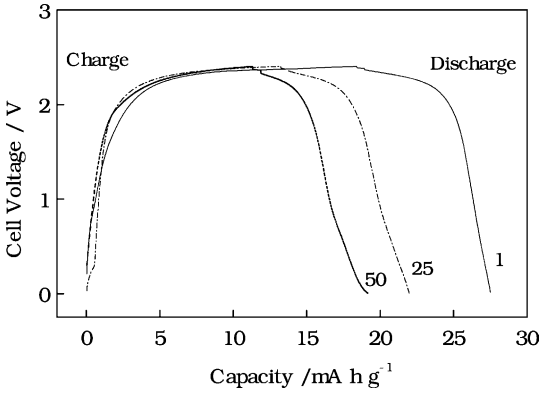


Fig. 4. Charge–discharge curve for the $LiMn_2O_4/LiTi_2O_4$ cell cycled at 0.1 mA/cm$^2$ in PC–THF electrolyte for various cycles. Cycle numbers are indicated in the figure.

10 cycles, reflecting a 60% loss of reversibility. Hence, on repeated cycling, the extraction and insertion process of Li ions into the structure of $LiMn_2O_4/LiTi_2O_4$ is not reversible. As this is an oxide–oxide battery system, at this stage it is difficult to draw a conclusion on the irreversibility, however the influence of the large second phase $Li_2Ti_3O_7$ in the negative electrode may play a role in the capacity decay. From the nature of the charge–discharge curves it is evident that the $LiMn_2O_4/LiTi_2O_4$ cell can be used as a 2.3 V rechargeable battery, if there is an improvement in capacity.

In order to improve the performance of the battery in terms of capacity, an attempt was made to examine another low viscosity mixed solvent $LiClO_4$ with PC–THF as electrolyte. Using this electrolyte, the $LiMn_2O_4/LiTi_2O_4$ cell was measured at room temperature and ambient atmosphere. It was noted that, Li cyclic efficiency increased in this electrolyte and the cyclic performance was slightly improved. The electrochemical charge and discharge curves for $LiMn_2O_4/LiTi_2O_4$ at a current density of 0.1 mA/cm$^2$ in PC–THF electrolyte (Fig. 4) show that the capacity of this cell for the first cycle was 27 mAh/g, which was twice that in EC–PC electrolyte, but still this is a very low value compared to other intercalation compounds. This increase in capacity could be explained by the presence of the low viscosity solvent electrolyte (THF) that increases the conductivity and Li cycling efficiency due to lower chemical reactivity of THF towards Li and a smaller practical $Li^+$ ion radius assuming $Li^+$–THF complex formation. The mixed solvent electrolyte $LiClO_4$–PC–THF which a has high $Li^+$ ion conductivity and also high Li cycling efficiency shows an improvement in cycling behavior of 50 cycles at a current density of 0.1 mA/cm$^2$ while that of only 10 cycles for the $LiClO_4$–EC–PC mixed solvent. The voltage versus capacity curves for the 25th and 50th cycles of a cell cycled in PC–THF showed capacity retention during cycling. The THF-containing electrolyte shows a better performance to repeated lithium insertion and extraction than the EC–PC electrolyte although the capacity was not appreciably improved. The improvement in the cycling behavior is attributed to the mixed effects of a high dielectric constant of PC (preventing ionic association at high solute concentration), low viscosity of THF (increasing migration rate) and $Li^+$ ion selective solvation of THF.

Although, the use of mixed solvents given some improvement in performance, advances in material preparation are also necessary to improve the rate capabilities and long-term capacity of these materials. A thorough review of preparation procedures of titanium spinel, $LiTi_2O_4$, is in progress. This material shows (Fig. 2) a large amount of second phase, $Li_2Ti_3O_7$, which contains fully oxidized $Ti^{4+}$, whereas the mean oxidation state of Ti in $LiTi_2O_4$ $3.5^+$. Hence, this material should be carefully synthesized to maintain the average oxidation of >3.5 so the redox potential during the electrochemical process will be stable thereby increasing the capacity of the electrode. Further investigation of the synthesis of both of these oxides underway.

## 4. Conclusion

The possibility of using the intercalation compound $LiTi_2O_4$ as a replacement for metallic lithium in secondary lithium batteries was studied. The average cell voltage for this "rocking chair" battery was found to be 2.3 V. For practical applications, a rocking chair battery should have good reversibility and a reasonable potential difference between the two electrodes. The problems associated with metallic lithium were solved at the expense of lowering the overall cell voltage. In this type of intercalation cell, electrodes 1 mm thick could be made and could be discharged to 0 V.

The electrochemical behavior of these cells was tested at low current density with mixed solvents as electrolytes. It was found that in EC–PC electrolyte, the extraction and insertion process was not efficient on repeated cycling even though EC had many desirable properties. When THF was used instead of EC, the cycling behavior was improved, which was attributed to the mixed effects of the high dielectric constant of PC, low viscosity of THF and $Li^+$ ion selective solvation of THF. Since this type of battery contains no metallic lithium, it is expected to be fairly safe and reliable for a wide range of applications. With improvements in capacity, materials such as these could improve the overall performance of secondary lithium intercalation cells.

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