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May 2000

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**Improved Discharge Characteristics of Tunnel-Containing Manganese
Oxide Electrodes for Rechargeable Lithium Battery Applications**

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Improved Discharge Characteristics of Tunnel-containing Manganese Oxide Electrodes for Rechargeable Lithium Battery Applications

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Abstract

Li_xMnO_2 made from $\text{Na}_{0.44}\text{MnO}_2$ has an unusual tunnel structure which allows ion insertion processes to occur with minimal strain. It cycles very reversibly at an average voltage of about 3.2 vs. Li without undergoing phase conversion. The stability of this material makes it a promising candidate for use in electric vehicle applications, which not only have severe cost constraints, but also require long cycle life and abuse-tolerance. In practical lithium cells, however, the demonstrated capacity is typically less than the predicted 200 mAh/g for Li_xMnO_2 cathode materials made by conventional solid-state reactions. This is due to kinetic limitations and to the sloping discharge characteristics. Attritor-milling of conventionally-made Li_xMnO_2 and glycine-nitrate combustion synthesis have been used to produce powders with average particle size below 1 μm , improved rate capability, and a 15% improvement in utilization. Up to 55% of the Mn in Li_xMnO_2 with the $\text{Na}_{0.44}\text{MnO}_2$ structure can also be replaced with Ti. Ti-doped analogs have modified discharge characteristics, with some exhibiting better utilization between set voltage limits than the parent compound.

Introduction

Lithium ion-exchanged materials made from $\text{Na}_{0.44}\text{MnO}_2$ have recently been used as positive electrodes in rechargeable lithium battery configurations.^{1,2,3} These cathodes show a high degree of reversibility towards intercalation processes and are unusually resistant to degradation when over-charged or over-discharged.⁴ Furthermore, conversion to the thermodynamically favored spinel structure does not occur below about 400°C , nor does degradation occur upon cycling at elevated temperatures. $\text{Na}_{0.44}\text{MnO}_2$ has an unusual double tunnel structure that can accommodate intercalation and de-intercalation of either Na or Li ions without undue stresses, rendering it extremely robust (Figure 1). This makes it attractive for use in electric vehicle batteries, in which abuse situations such as over-charging and -discharging are likely to occur.

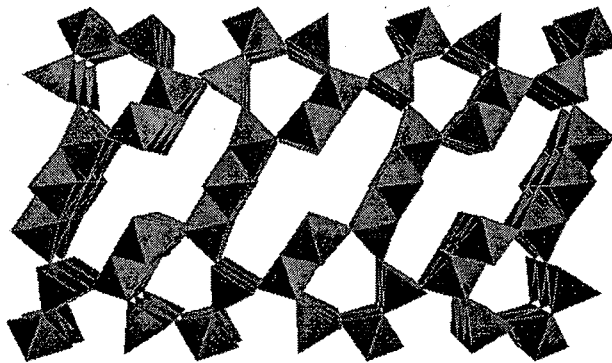


Figure 1. Structure of Li_xMnO_2 made from $\text{Na}_{0.44}\text{MnO}_2$, looking down the c-axis.

$\text{Na}_{0.44}\text{MnO}_2$ is readily made by reacting together solid state precursors at elevated temperatures. The material may be used as-is, or ion-exchanged prior to use in a lithium battery configuration. Partial substitution of Li for Na occurs under mild conditions, but full exchange occurs in molten salt solutions above 200° C. The products are iso-structural to the parent compound.²

All sites in the tunnels are full at a composition of $\text{Na}_{0.66}\text{MnO}_2$, corresponding to ~200 mAh/g theoretical capacity for reversible sodium intercalation. In theory, higher capacities may be possible in lithium batteries because of the smaller size of the Li^+ ion. In operating Li cells with liquid or polymer electrolytes, the shape of the discharge profile varies with extent of exchange and determines utilization between set voltage limits. Voltage limits are selected for compatibility with solvents and electrolytes and to minimize power loss during operation. The discharge profile is steeper for highly exchanged samples, effectively decreasing utilization. Although sodium-containing materials have better discharge characteristics, *in situ* exchange processes cause a slow apparent capacity fade, which is undesirable.

To maintain the good cycling characteristics inherent to materials with the $\text{Na}_{0.44}\text{MnO}_2$ while improving the discharge capacity, we have taken several approaches. One is to modify the voltage profile by substituting some of the Mn with Ti. The second is to engineer particle size and morphology by various means, in order to maximize rate capability and utilization. Herein, we describe preliminary results with these approaches.

Experimental

$\text{Na}_{0.44}\text{Ti}_y\text{Mn}_{1-y}\text{O}_2$ compounds with $y=0, 0.11, 0.22, 0.33, 0.44$ and 0.55 were made by heating together well-mixed powders of $\text{Na}_2\text{Ti}_3\text{O}_7$, Mn_2O_3 and Na_2CO_3 in the desired proportions at 850°C for ten hours. Best results were obtained when a slight excess of Na ($0.47\text{-}0.5$ Na/M, where $M=\text{Mn}+\text{Ti}$) was used, due to some loss of sodium during heating. In cases where Mn_2O_3 impurities were still detected, powders were re-ground with NaOH and re-fired. The products obtained after this treatment were phase-pure according to the x-ray powder diffraction patterns (obtained with a Siemens D5000 diffractometer), and were black or brown-black in color. Some powders were ground eight hours in an attritor mill prior to use in electrochemical cells. Alternatively, $\text{Na}_{0.44}\text{MnO}_2$ was synthesized by a glycine-nitrate combustion synthesis technique.⁵

$\text{Na}_{0.44}\text{Ti}_y\text{Mn}_{1-y}\text{O}_2$ powders were ion-exchanged by heating them in a molten salt mixture of 68 mol% LiNO_3 /32 mol% KNO_3 at 230°C . A 2-5-fold excess of the Li salt was used, and the mixture was poured out and replaced twice during the exchange, which typically took 48 hours. Exchanges were determined to be complete by XRD analysis.

Cells were assembled by stacking porous electrodes containing the active material, C black and EPDM binder on stainless steel or graphite foil discs, Celgard 3401, lithium metal (Cyprus-Foote Mineral Co., Kings Mountain, NC), metal backing plates, and wave washers in 2032 coin cells and pressing together, after wetting with electrolyte solution (1M LiPF_6 in 1:2 EC/DMC, EM Industries, Darmstadt, Germany). Composite polymer electrodes and polymer cells were fabricated as described previously.¹ Polymer cells were equilibrated at $85\pm 0.5^\circ\text{C}$ in a convection oven equipped with a Eurotherm

controller for at least one hour prior to testing. A MacPile II from Bio-Logic, SA, Claix France was used for both galvanostatic and potentiostatic experiments. For electrochemical potential spectroscopy experiments (ECPS), the potential was stepped 10 mV every 4 hours, or until the current had decreased to 1/1000 of its initial value, between 2.5 and 3.5V for polymer cells and between 2.5 and 3.8 V for liquid electrolyte cells. Relative diffusion coefficients were determined from i vs t data for each step by applying the Cottrell equation. The actual contact area between the active material in the porous electrodes and the electrolyte solution is unknown; therefore it is not possible to correlate these values with true diffusion coefficients.

Results and Discussion

ECPS experiments indicate that Li insertion into Li_xMnO_2 with the $\text{Na}_{0.44}\text{MnO}_2$ structure is completely reversible above 2.5V vs. Li, but relative diffusion coefficients decrease markedly both at the end of discharge and above 3.3V vs. Li in liquid electrolyte cells (Figure 2). For materials made by solid state synthesis, utilization at moderate rates is less than that predicted by integration of the data from the ECPS experiment (Figure 3). These observations indicate that slow kinetics prevent full utilization during discharge. In contrast, attritor-milled material or Li_xMnO_2 made from $\text{Na}_{0.44}\text{MnO}_2$ produced by a glycine-nitrate combustion process (GNP- Li_xMnO_2) deliver the expected capacity at 0.5-1 mA/cm².

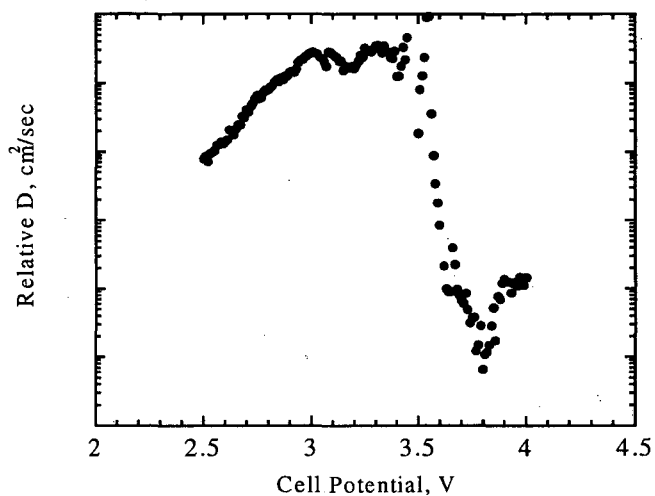


Figure 2. Relative diffusion coefficients determined from a stepped potential experiment on a Li/EC-DMC, 1M LiPF₆/Li_xMnO₂ cell at room temperature.

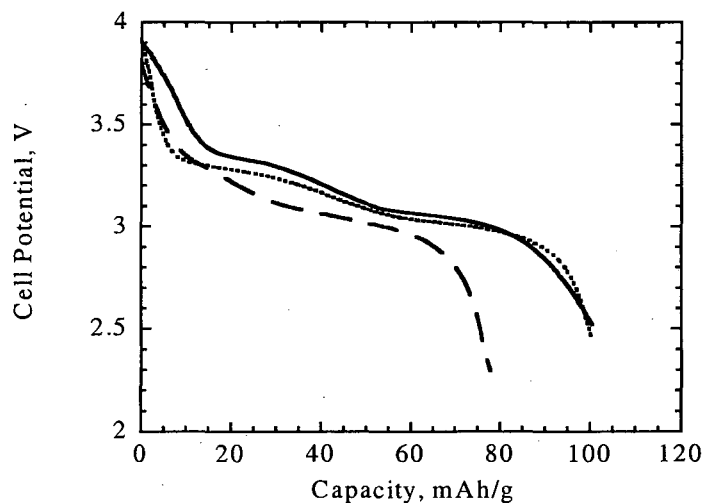


Figure 3. Pseudo-open circuit potential (—) of a Li/EC-DMC, 1M LiPF₆/Li_xMnO₂ cell at room temperature. Discharges at 0.5 mA/cm² of Li/EC-DMC, 1M LiPF₆ cells containing conventionally prepared Li_xMnO₂ (---) and GNP-Li_xMnO₂ (.....).

Diffusion is enhanced in materials with sub-micron sized particles, and the overpotential is decreased, allowing full utilization during discharge. The improved utilization does not come at the expense of cyclability, however, since cells with attritor-milled or GNP- Li_xMnO_2 cycle without losses (Figure 4). This is particularly significant, since LiMn_2O_4 with high surface area tends to exhibit capacity fading due to the enhanced rate of side-reactions (e.g., oxidation of electrolyte).

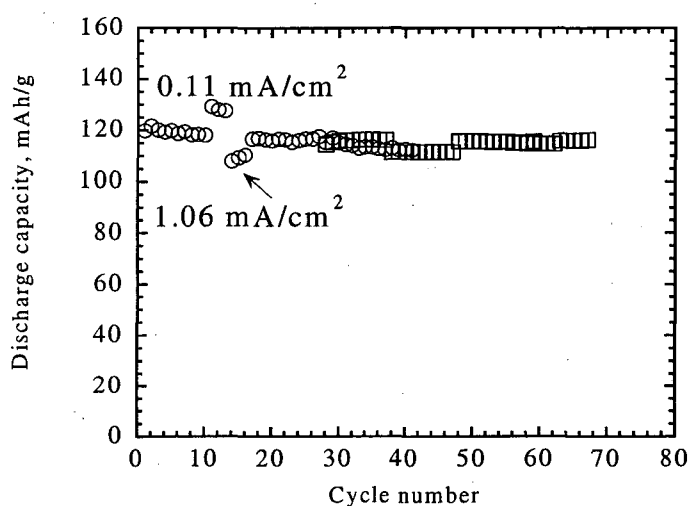


Figure 4. Capacity as a function of discharge number for a Li/EC-DMC, 1M LiPF_6 /attritor-milled Li_xMnO_2 cell (O) at room temperature between 4.0 and 2.35V at 0.53 mA/cm^2 (except where otherwise noted), and a Li/EC-DMC, 1M LiPF_6 /GNP- Li_xMnO_2 cell (□) between 4.2 and 2.5 V (discharges 38-47 between 4.1 and 2.5V) at 0.13 mA/cm^2 . The first 28 cycles are omitted for clarity.

A similar improvement in performance is seen in Li/P(EO)₈LiTFSI/GNP- Li_xMnO_2 cells at 85° C. These cells deliver 95-100 mAh/g between 3.6 and 2.5V at 1.5C rate,

and have been cycled over 140 times without any capacity loss. The ability to cycle well at elevated temperatures is another unusual and desirable feature of this material.

The stability, high rate capability, and excellent cycling characteristics of Li_xMnO_2 made from $\text{Na}_{0.44}\text{MnO}_2$ make it a good candidate for applications needing abuse-tolerance, long life, and excellent reversibility, such as power-assist batteries for hybrid electric vehicles. High energy densities are not needed in such systems, but materials in these cells must be very low cost and must be able to withstand a number of abuse situations, such as over-charging, over-discharging, and temperature excursions. At present, no other manganese oxide has these needed characteristics.

For most other applications, including electric vehicle uses, the demonstrated energy density of this cathode material is, at present, too low. Only about 50-60% of the available capacity is utilized even in the improved Li_xMnO_2 because not all the Li ions can be extracted in a practical potential range. To modify the discharge characteristics, we have made a series of Ti-substituted materials, $\text{Li}_x\text{Ti}_y\text{Mn}_{1-y}\text{O}_2$, with $y=0.11, 0.22, 0.33, 0.44,$ and 0.55 , having the $\text{Na}_{0.44}\text{MnO}_2$ structure. Electrochemical potential spectroscopy experiments on polymer electrolyte cells at 85°C indicate that Ti-doped materials have somewhat different discharge characteristics (Figure 5). The two potential plateaux at about 3.3 and 3.1 V vs Li that are evident in the OCP profile of Li_xMnO_2 are largely absent in the Ti-doped materials, which have more gradually sloping profiles. For $y=0.11, 0.33,$ and 0.44 , capacities between 3.5 and 2.5V are similar to that found for Li_xMnO_2 , but higher capacity is obtained for $y=0.22$, and significantly less capacity for $y=0.55$. Substitution of Ti for Mn in the $\text{Na}_{0.44}\text{MnO}_2$ structure increases the unit cell size and may allow access to more Li ion sites, as

occurs when sodium ions are left in undoped materials, where they prop open the tunnels. It is, however, likely that Ti is not electro-active in the potential range used, thus a high level of substitution counter-acts the beneficial effect of the unit cell size increase and reduces capacity. The 22% Ti-doped material represents a compromise between the two effects.

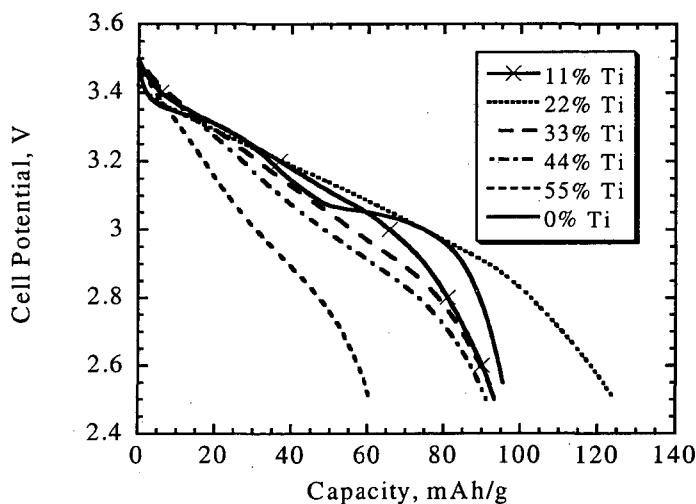


Figure 5. Pseudo-open circuit potential profiles of $\text{Li}/\text{P}(\text{EO})_8\text{LiTFSI}/\text{Li}_x\text{Ti}_y\text{Mn}_{1-y}\text{O}_2$ cells at 85°C .

Excellent cycling behavior is retained for the higher capacity $\text{Li}_x\text{Ti}_{0.22}\text{Mn}_{0.78}\text{O}_2$ electrode in a polymer cell configuration at 85°C . (Compare results for attritor-milled Li_xMnO_2 and $\text{Li}_x\text{Ti}_{0.22}\text{Mn}_{0.78}\text{O}_2$ discharged at the same rate in Figure 6). Less capacity fading is, however, seen for $\text{Li}_x\text{Ti}_{0.33}\text{Mn}_{0.67}\text{O}_2$ and GNP- Li_xMnO_2 electrodes, even though the latter was discharged at a higher rate. In the case of GNP- Li_xMnO_2 , the small particle size enhances the rate of Li^+ diffusion, allowing higher current densities to be used. There is also less likelihood of inadvertent over-reduction of Li_xMnO_2 at high

current densities or near the end of discharge when diffusion is fast. (It has been shown that a slow phase change that eventually causes a fall-off in performance of this electrode occurs when the OCP falls below about 2.5V vs. Li).² It is, therefore, likely that inadvertent over-discharge is primarily responsible for the fade rate of about 0.2% per cycle for the cell containing attritor-milled Li_xMnO_2 even though discharges were stopped when the cell potential reached 2.5V. The over-discharge characteristics of $\text{Li}_x\text{Ti}_y\text{Mn}_{1-y}\text{O}_2$ electrodes are, at present, unknown, but they appear to be more resistant to damage than the parent compound; $\text{Li}_x\text{Ti}_{0.22}\text{Mn}_{0.78}\text{O}_2$ does not lose capacity faster than Li_xMnO_2 even though it was discharged to a lower voltage (2.4), and $\text{Li}_x\text{Ti}_{0.33}\text{Mn}_{0.67}\text{O}_2$ exhibits no losses upon cycling, although the rate capability is not as good as for GNP- Li_xMnO_2 .

Lower capacity is seen in Ti-doped materials when they are discharged at rates greater than about C/3 in Li/polymer cells, or when they are used in liquid electrolyte cells at room temperature. It is likely that synthetic methods which produce high surface area/small particle size products will aid diffusion and increase the rate capability of these materials, as they did in the case of Li_xMnO_2 .

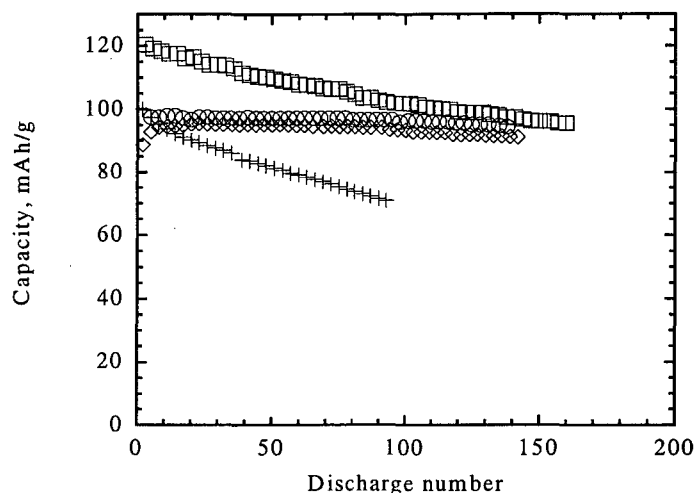


Figure 6. Capacity as a function of cycle number for $\text{Li}/\text{P}(\text{EO})_8\text{LiTFSI}/\text{Li}_x\text{Ti}_y\text{Mn}_{1-y}\text{O}_2$ cells at 85°C . Discharges were carried out at $0.1\text{ mA}/\text{cm}^2$ for attritor-milled Li_xMnO_2 (+) and $\text{Li}_x\text{Ti}_{0.33}\text{Mn}_{0.67}\text{O}_2$ (\diamond) between 3.6 and 2.5 V and $\text{Li}_x\text{Ti}_{0.22}\text{Mn}_{0.78}\text{O}_2$ (\square) between 3.6 and 2.4V. Discharges were carried out at $0.5\text{ mA}/\text{cm}^2$ for GNP- Li_xMnO_2 (\circ) between 3.6 and 2.5V.

Conclusions

Li_xMnO_2 and $\text{Li}_x\text{Ti}_y\text{Mn}_{1-y}\text{O}_2$ electrodes with the $\text{Na}_{0.44}\text{MnO}_2$ structure are highly reversible towards Li intercalation processes, and cycle well in either Li/liquid electrolyte or Li/polymer electrolyte cell configurations at elevated temperatures. Materials with improved rate capability can be produced by solution synthetic techniques or by attritor-milling. Substitution of some of the Mn with Ti increases capacity between set voltage limits without compromising the cycling characteristics.

Acknowledgments

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