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for Alkali Metal Polymer Batteries**

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# ELECTROCHEMICAL CHARACTERIZATION OF ORTHORHOMBIC $\text{Na}_x\text{MnO}_2$ FOR ALKALI METAL POLYMER BATTERIES

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## Introduction

It has recently been shown<sup>1</sup> that orthorhombic  $\text{Na}_x\text{MnO}_2$  can be used as a positive electrode for secondary alkali metal batteries. Intercalation of lithium or sodium ions occurs reversibly over wide ranges of composition (approximately 0.5 Na/Mn or 0.6 Li/Mn) at potentials compatible with the use of solid polymer electrolytes such as poly(ethylene) oxide. No structural changes have been detected in either sodium or lithium cells after 50 or more cycles, and the sloping voltage profiles suggest that the system remains single phase during charge and discharge. The complexity of the x-ray diffraction powder patterns for orthorhombic  $\text{Na}_x\text{MnO}_2$  makes interpretation of the intercalation processes difficult, however. Electrochemical potential spectroscopy (ECPS), a technique in which the potential of cells is slowly stepped and the current or charge measured as a function of time may be used to obtain structural information on intercalation compounds. In this study, we report the results of ECPS experiments on Na/PEO/ $\text{Na}_x\text{MnO}_2$  cells and interpret them in terms of the structure of  $\text{Na}_x\text{MnO}_2$ .

## Experimental

Orthorhombic  $\text{Na}_x\text{MnO}_2$  for use in electrochemical cells was synthesized by heating together well-mixed samples of sodium permanganate and  $\text{Mn}_2\text{O}_3$  at 800° C in air for eight hours. The stoichiometries of the starting materials were chosen so that the product would have an approximate composition of  $\text{Na}_{0.44}\text{MnO}_2$ . The resulting black powder was dry ball-milled for four hours prior to use in sodium cells. Elemental analyses were carried out by the University of California at Berkeley Microanalytical Laboratory (Berkeley, CA). Samples were stirred in aqueous hydrochloric acid solution at room temperature for twelve hours in order to oxidize them. The products were filtered, washed well with de-ionized water and dried under vacuum.

Composite cathodes containing 30 w/o active material, acetylene black, poly(ethylene oxide) (P(EO)) and sodium trifluoromethanesulfonate (NaTf) and separators with composition P(EO)<sub>20</sub>NaTf were prepared as described previously<sup>2</sup>. Sodium metal was purified and extruded into thin foils for use as anodes in cells for ECPS and galvanostatic charging and discharging experiments. Cells were assembled and heated to 85° C for at least one hour prior to testing under an inert atmosphere. A MacPile II from Bio-Logic SA (Claix, France) was used for the electrochemical experiments. X-ray powder patterns were obtained with a Siemens diffractometer.

## Results and Discussion

Elemental analyses on the product of the reaction between sodium permanganate and  $\text{Mn}_2\text{O}_3$  indicated a Na/Mn ratio of 0.38, with a Mn content slightly higher than expected for  $\text{Na}_{0.38}\text{MnO}_2$ . The XRD pattern (Figure 1, lower spectrum) shows a small amount of  $\text{Mn}_2\text{O}_3$  impurity (marked with an asterisk). Treatment of orthorhombic  $\text{Na}_x\text{MnO}_2$  with aqueous acid in air removes  $\text{Mn}_2\text{O}_3$ , and oxidizes it, giving  $\text{Na}_{0.2}\text{MnO}_2$  as the product. The XRD pattern (upper spectrum, Figure 1) is altered from that of the precursor, although it clearly shares similarities. In particular, numerous peaks are shifted to higher values of  $2\theta$ , indicating a decrease in the size of the unit cell. This is consistent with oxidative de-intercalation.

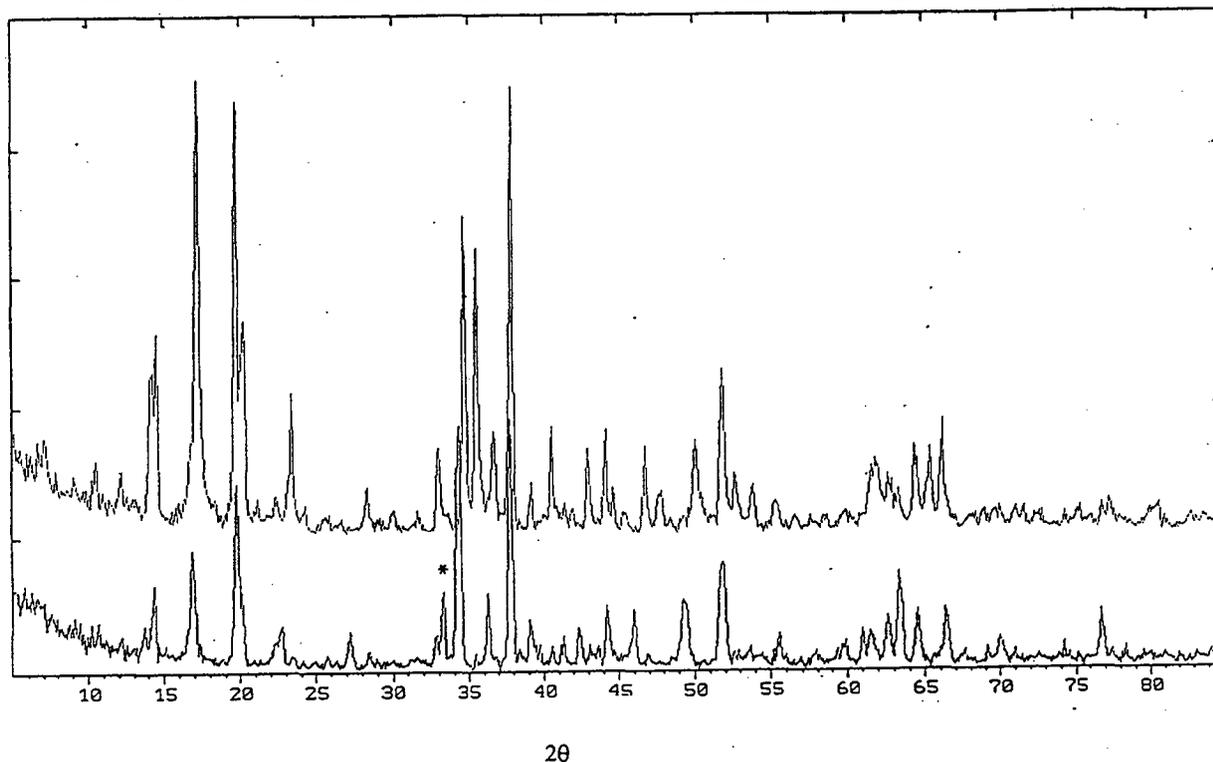


Figure 1. XRD powder patterns of " $\text{Na}_{0.38}\text{MnO}_2$ " (bottom) with  $\text{Mn}_2\text{O}_3$  contaminant marked by an asterisk, and  $\text{Na}_{0.2}\text{MnO}_2$  (top) prepared by an acid-catalyzed air oxidation of  $\text{Na}_x\text{MnO}_2$ . This treatment also removes the  $\text{Mn}_2\text{O}_3$  impurity.

Orthorhombic  $\text{Na}_{0.44}\text{MnO}_2$ , first reported in 1971<sup>3</sup>, has been indexed only by analogy to  $\text{Na}_4\text{Mn}_4\text{Ti}_5\text{O}_{18}$  from single crystal data obtained by Mumme.<sup>4</sup> Figure 2 shows an idealized representation of the structure.  $\text{Na}_{0.44}\text{MnO}_2$  contains both  $\text{MnO}_6$  octahedra and  $\text{MnO}_5$  square pyramids linked together by edges and corners to form large S-shaped tunnels and smaller tunnels similar to those found in calcium ferrite. The unusual structural features may account for both the observed thermal stability of this compound and the meta-stability during intercalation and de-intercalation at low temperatures. Considerable bond-breaking and re-arrangement may be required to convert orthorhombic  $\text{Na}_x\text{MnO}_2$  to thermodynamically favored phases such as  $\text{LiMn}_2\text{O}_4$  (e.g., during discharge in lithium cells) or other sodium manganese oxides.

When the Na/Mn ratio is 0.44, the small tunnels are completely filled with sodium ions, and the large tunnels are half-way filled (two sodium ions per tunnel). Complete filling (e.g., four sodium ions in each large tunnel) should give  $\text{Na}_{0.66}\text{MnO}_2$  (fully reduced state).

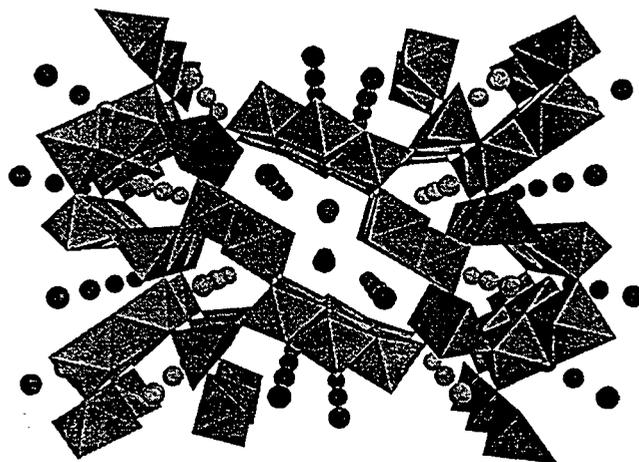


Figure 2. An idealized representation of orthorhombic Na<sub>x</sub>MnO<sub>2</sub> showing MnO<sub>6</sub> octahedra and MnO<sub>5</sub> square pyramids. Sites for sodium ions are indicated by spheres.

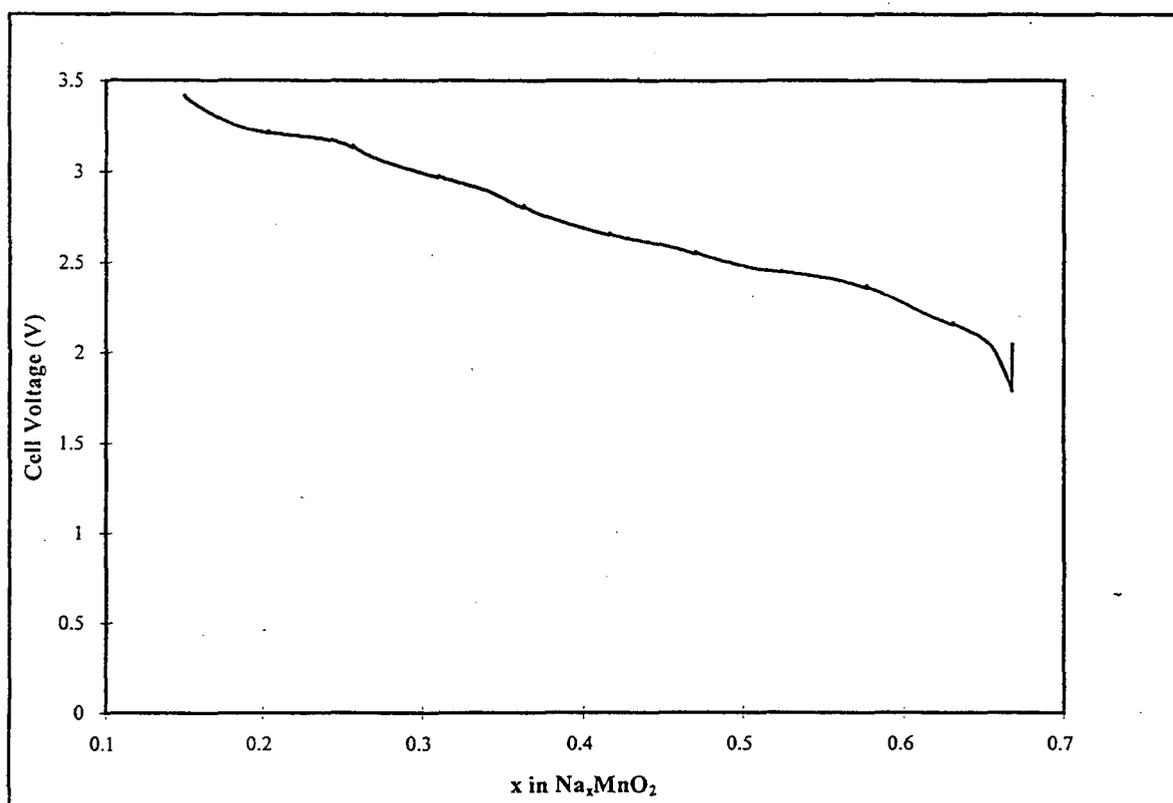


Figure 3. A galvanostatic discharge of a Na/P(EO)<sub>20</sub>NaTf/Na<sub>x</sub>MnO<sub>2</sub> cell at 0.1 mA/cm<sup>2</sup> and 85 degrees. (The small spikes in the profile are due to intermittent open circuit periods lasting several seconds each). The cell was assembled in the partially discharged state (x in Na<sub>x</sub>MnO<sub>2</sub> approximately equal to 0.38) and charged to 3.5 V before this data was obtained (not shown).

Galvanostatic titration in sodium cells<sup>1</sup> led to an estimated composition of Na<sub>0.66-0.75</sub>MnO<sub>2</sub> at the end of discharge; approximately within experimental error. (The presence of Mn<sub>2</sub>O<sub>3</sub> in the cathode active material introduces a degree of uncertainty). Sodium in the large tunnels should be more readily removed than from the small ones; a composition of Na<sub>0.22</sub>MnO<sub>2</sub> is expected if

only the small tunnels are full. Electrochemical oxidation of  $\text{Na}_{0.44}\text{MnO}_2$  can be accomplished reversibly to a composition of  $\text{Na}_{0.15-0.2}\text{MnO}_2$ ; the limit is determined primarily by the oxidative decomposition of the poly(ethylene oxide)/NaTf electrolyte. The electrochemical and chemical oxidations indicate that it is possible to remove at least some sodium from the small tunnels. Complete removal may be possible with use of stronger oxidizing agents or more stable electrolytes in electrochemical cells, but this has not yet been carried out.

Figure 3 shows a typical discharge curve of a Na/PEO/ $\text{Na}_x\text{MnO}_2$  cell at moderate current densities. The profile is generally sloping, suggestive of a single phase system, but several small plateaux are discernible. At this rate, kinetic effects mask the true open circuit voltages, making structural correlations difficult. It is common to subject cells to very slow galvanostatic discharges (often less than  $C/100$ ), and long open circuit periods to obtain thermodynamic data. Peaks in the  $dQ/dV$  curves can then be correlated with phase or ordering transitions, and information obtained about sites of occupancy during ion insertion and removal. *In situ* XRD experiments may also be used to observe intercalation processes directly. Both of these methods are extremely demanding in terms of time and instrument capability, however.  $dQ/dV$  data may be obtained more quickly using electrochemical potential spectroscopy (ECPS). In this method, the cell potential is stepped incrementally, and current or charge recorded as a function of time. The next step is taken only when the current has decayed to a fraction (typically, 1/100th) of the initial value<sup>5</sup>. ECPS is particularly useful for interpreting insertion processes into materials that are poorly crystalline or have complex XRD patterns, as in the present case, and has been used successfully to interpret proton intercalation into  $\gamma/\epsilon \text{MnO}_2$ <sup>6</sup>.

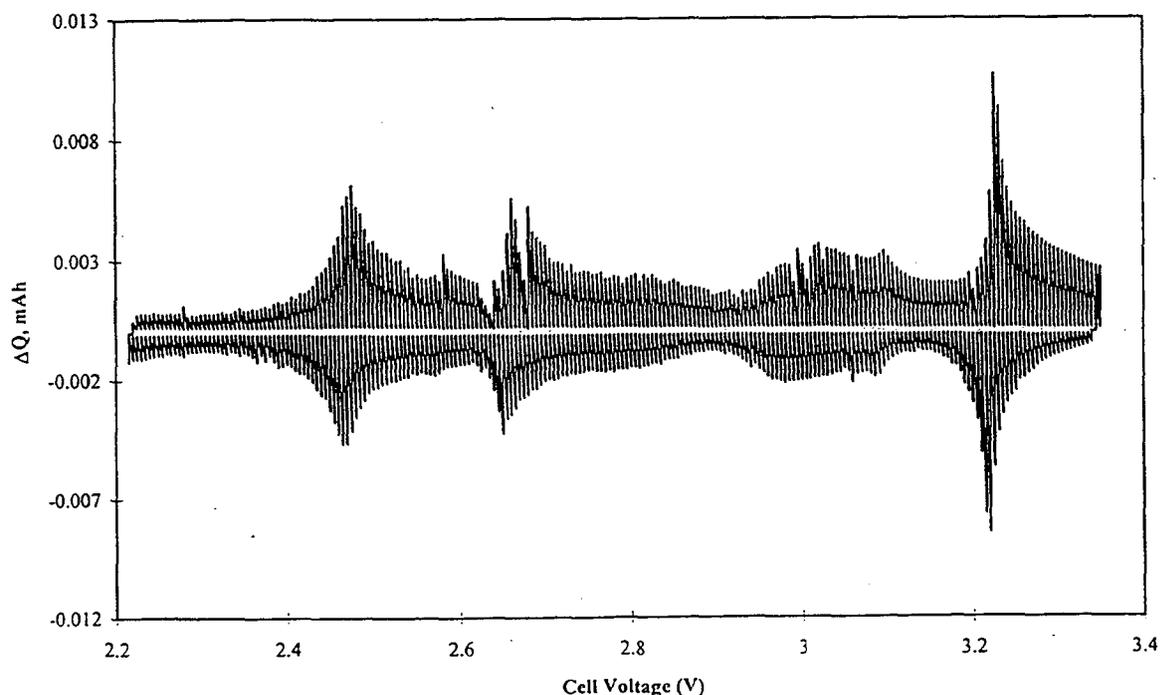


Figure 4. Electrochemical potential spectrum of a discharged Na/P(EO)<sub>20</sub>NaTf/ $\text{Na}_x\text{MnO}_2$  cell at 85°C. The potential was stepped in 5 mV increments between 2.215 and 3.350 V, and then reversed. The current was allowed to decay to 1/100th of the initial value between steps.

Figure 4 shows an ECPS trace of a Na/P(EO)<sub>20</sub>NaTf/Na<sub>x</sub>MnO<sub>2</sub> cell obtained on its second cycle. The experiment took approximately three weeks to complete and indicates that the system is highly reversible. A slightly greater amount of current is passed during oxidation of Na<sub>x</sub>MnO<sub>2</sub> than during reduction; this is noticeable at the high voltage end of the charge profile (upper trace) and may be attributed to a slow irreversible oxidation of the electrolyte. No other irreversible process is detected, indicating that corrosion (e.g., at the sodium/current collector or sodium/PEO interfaces) is not occurring under these conditions.

Integration of the charge passed during reduction allows x in Na<sub>x</sub>MnO<sub>2</sub> to be calculated at relevant points in the discharge, and is correlated with the ECPS features in the table below. As Na<sub>0.15</sub>MnO<sub>2</sub> is reduced, sodium ions are inserted into the small tunnels first. An ordering transition (peak) is seen at 3.22 V, at which point the small tunnels are completely occupied and the large tunnels are completely empty (Na<sub>0.22</sub>MnO<sub>2</sub>). Below 3.22 V, sodium ions enter the large tunnels, and preferentially fill one of the four possible sites until a composition of Na<sub>0.33</sub>MnO<sub>2</sub> is reached, near 3.05 V. Somewhat surprisingly, further insertion of ions appears to result in a disordered arrangement until three out of four of the sites in the large tunnels are filled (Na<sub>0.55</sub>MnO<sub>2</sub>) resulting in a sharp peak at 2.65 V. The ordering transition for occupation of the all four sites in the large tunnel (2.46 V) occurs slightly before the composition Na<sub>0.66</sub>MnO<sub>2</sub> is reached; in practice, it may be difficult to fill the tunnels completely due to inter-ion repulsion.

Table 1: Site Occupancy in Na<sub>x</sub>MnO<sub>2</sub> as a Function of State of Charge.

Expected composition	Occupancy	% intercalated (calculated) <sup>a</sup>	Cell Voltage (V), from ECPS data	% intercalated (observed from ECPS)
Na <sub>0.15</sub> MnO <sub>2</sub>	large tunnels empty, small tunnels partially filled	0%	3.35, no feature	0%
Na <sub>0.22</sub> MnO <sub>2</sub>	small tunnels filled, large tunnels empty	14%	3.22, sharp peak	13%
Na <sub>0.33</sub> MnO <sub>2</sub>	small tunnels filled, large tunnels 1/4 full	35%	3.05, broad feature	37%
Na <sub>0.55</sub> MnO <sub>2</sub>	small tunnels filled, large tunnels 3/4 full	78%	2.65, sharp peak	78%
Na <sub>0.66</sub> MnO <sub>2</sub>	both small and large tunnels completely full	100%	2.46, sharp peak	91%

a) The composition Na<sub>0.15</sub>MnO<sub>2</sub> is assumed for the fully charged state, based upon the coulometry experiments.

## Conclusions

Electrochemical potential spectroscopy has been used successfully to observe and explain ordering transitions in orthorhombic  $\text{Na}_x\text{MnO}_2$  as it is discharged in a sodium/polymer cell. Features can be assigned on the basis of sequential filling of sites in the small and then the large tunnels of the structure as the reduction progresses. Intercalation of lithium into  $\text{Na}_x\text{MnO}_2$  may be less straightforward than that of sodium, and is worthy of investigation by ECPS.  $\text{Li}/\text{Na}_x\text{MnO}_2$  cells have a greater discharge capacity than  $\text{Na}/\text{Na}_x\text{MnO}_2$  cells, suggesting that more than four lithiums per large tunnel can be inserted. (It is also possible, but less likely that more than one lithium can be placed inside the small tunnels). This implies that the sites for lithium occupancy might be somewhat different than that for sodium. Further investigation into the properties of orthorhombic  $\text{Na}_x\text{MnO}_2$  and its utility as a positive electrode for rechargeable sodium and lithium cells is presently underway in this laboratory.

## Acknowledgments

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