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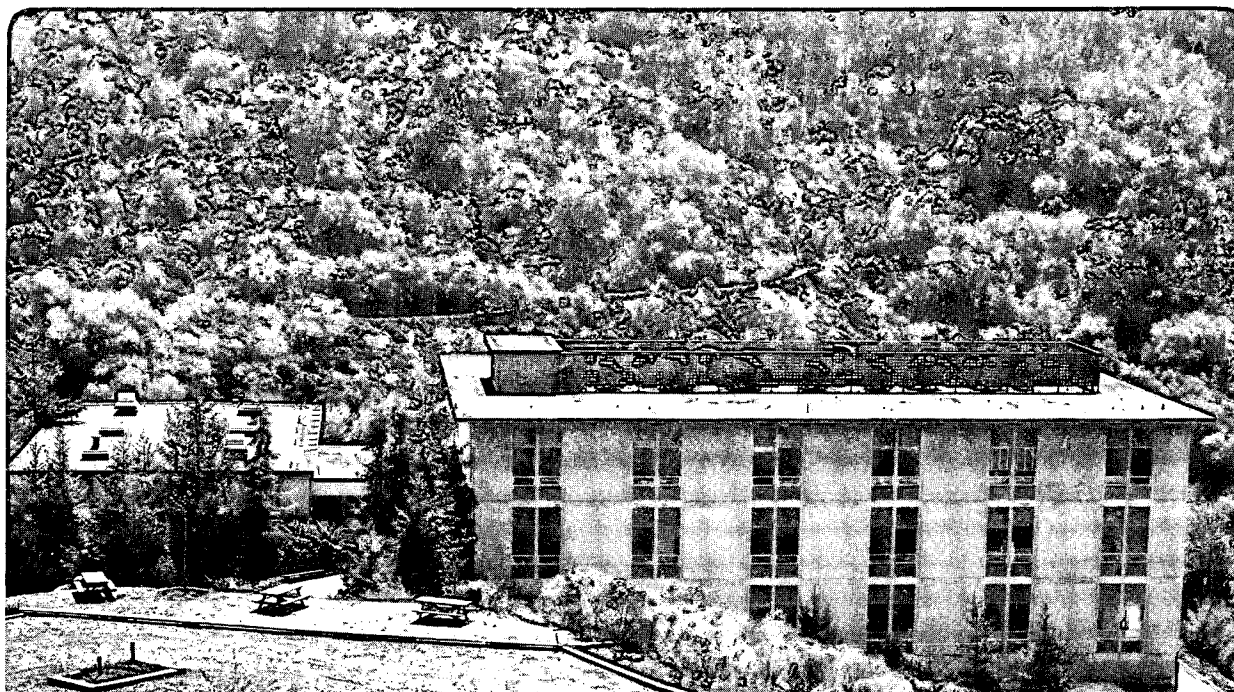# Lawrence Berkeley Laboratory
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Orthorhombic Na_xMnO_2 as a Cathode Material for Secondary Sodium and Lithium Polymer Batteries

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Orthorhombic Na$_x$MnO$_2$ as a Cathode Material for Secondary Sodium and Lithium Polymer Batteries

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Abstract

The use of orthorhombic Na_xMnO_2 as a cathode material for alkali metal polymer electrolyte batteries is described for the first time. This sodium manganese bronze has a tunnel structure and can reversibly intercalate up to 0.55-0.6 alkali metal ions (Li^+ or Na^+) per manganese at moderate current densities, corresponding to capacities of 160-180 mAh/g. Li/PEO/$Na_{0.2}Li_xMnO_2$ cells (PEO = poly(ethylene oxide)) to date have been cycled over ninety times at 0.1 mA/cm^2, with excellent capacity retention. Na/PEO/Na_xMnO_2 and Na_xMnO_2/PEO/Na_xMnO_2 cells have been cycled over sixty times to date at the same rate, showing moderate capacity fading.

Introduction

Alkali metal solid polymer electrolyte (SPE) batteries, recently proposed for use in electric vehicle applications, require the use of inexpensive, environmentally benign, and widely available cathode materials such as MnO_2 to meet the demands of the market. Manganese dioxide is polyphasic[1] and structures can be tailor-made for secondary battery applications by varying synthetic conditions and by inclusion of foreign ions such as lithium or potassium[2]. The spinel $LiMn_2O_4$, recently developed as a cathode for rechargeable lithium[3] and rocking chair[4] batteries, is an example of such a ternary compound; this material readily undergoes reversible lithium ion insertion and thus is suitable for use in secondary battery systems. Unfortunately, the upper

voltage plateau in $LiMn_2O_4$ is above the stability threshold of polymer electrolytes like PEO (poly(ethylene oxide)); the lower voltage plateau may be cycled[5], but only at the expense of decreased energy density and increased capacity fading. Other three-dimensional manganese oxides, particularly those with large tunnels into which ions can be readily inserted[6], may be more compatible in alkali metal solid polymer electrolyte systems and are worthy of investigation. One such material is orthorhombic Na_xMnO_2, first synthesized with the nominal composition $Na_{0.44}MnO_2$ by Parant et al. in 1971[7]. It was thought that this material would not undergo intercalative processes[8] and no study of its electrochemical properties has been undertaken until the present time. It is now shown that Na_xMnO_2 can not only accommodate lithium or sodium ions over a wide range of composition at voltages compatible with solid polymer electrolytes but is also highly reversible to both sodium and lithium insertion processes.

Experimental

$Na_{0.44}MnO_2$ was prepared by heating together sodium carbonate with Mn_2O_3 in the appropriate stoichiometric ratio at 800° C in air for twelve hours. The resultant black powders were either hand ground or ball-milled to an average particle size of 1 μm. Alternatively, powders were prepared by the glycine-nitrate method;[9] an aqueous solution containing manganese nitrate, sodium nitrate and glycine was heated until spontaneous combustion occurred. The product was then calcined at 800° C for four hours to remove organic impurities. This resulted in very fine powders that did not require further grinding (average particle size approximately 1 μm). The electrochemical properties did not vary substantially

with method of preparation, but the amount of Mn_2O_3 (present as an impurity) detected by X-ray diffraction differed somewhat from sample to sample. Several samples of $Na_{0.44}MnO_2$ were stirred in aqueous hydrochloric acid at room temperature for twenty-four hours to remove mobile sodium ions and Mn_2O_3, washed well and dried *in vacuo* or in air at elevated temperatures. Ion exchange of $Na_{0.44}MnO_2$ was carried out by stirring powders in acetonitrile containing a slight stoichiometric excess of $LiCF_3SO_3$ at room temperature. Elemental analysis indicated that exchange was essentially complete after twelve hours.

A Siemens x-ray diffractometer was used to obtain structural information on bulk powders and on composite cathodes. Elemental analyses were performed by the University of California at Berkeley Microanalytical Laboratory.

$NaCF_3SO_3$, $LiCF_3SO_3$ or $LiN(CF_3SO_2)_2$ was complexed with poly(ethylene) oxide for use as separators and in the composite cathodes. A detailed description of the fabrication of components and cell testing is given elsewhere[10]. For open circuit voltage data, cells were allowed to rest for a minimum of four hours after current had passed before readings were taken.

Results and Discussion

Sodium polymer cells were assembled with cathodes containing either $Na_{0.44}MnO_2$ or $Na_{0.2}MnO_2$ (obtained from acid treatment of $Na_{0.44}MnO_2$). Figure 1a shows open circuit voltages as a function of composition for several examples at 85° C, as well as galvanostatic discharge curves. The OCV profile is sloping, suggesting that no phase changes occur during sodium insertion/de-insertion. X-ray powder diffraction patterns obtained on fully charged, halfway charged and

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fully discharged composite cathodes are consistent with this observation, showing slight shifting of peaks due to changes in the unit cell parameters. $Na_{0.44}MnO_2$ is in the approximately half-way discharged state and gives an OCV of about 2.9 vs. Na prior to charge. Reversible intercalation of sodium occurs over a range of $x=0.2-0.75$ in Na_xMnO_2, corresponding to a specific theoretical capacity of 163 mAh/g. At x greater than 0.75 it becomes increasingly difficult to pass current, and discharge past this point results in a deterioration of performance on subsequent cycles. The fully charged state corresponds to $x=0.2$ at 3.45 V vs. Na. Acid-treated sodium manganese oxide also gives an initial open circuit voltage reading of 3.45 V vs. Na, and exhibits identical discharge characteristics. Elemental analysis indicated that the composition of the acid-treated material is $Na_{0.2}MnO_2$ and x-ray diffraction experiments indicate that the chemically and electrochemically obtained $Na_{0.2}MnO_2$s are structurally identical. Several open circuit readings as a function of composition for the acid-treated material are included in figure 1a and show good agreement with those obtained from the charged and discharged $Na_{0.44}MnO_2$ cells.

Figure 1b shows open circuit voltage readings for cells containing lithium anodes, $P(EO)_8LiCF_3SO_3$ separators and cathodes containing the chemically produced $Na_{0.2}MnO_2$ at 105° C. The OCVs for undischarged cells were typically about 3.7 V, and approximately 0.6 Li/Mn could be inserted into this material reversibly from 3.7 to 2.5 V, corresponding to a specific theoretical capacity of 180 mAh/g. Again, the voltage profile is sloping, implying that no phase change occurs during intercalation/deintercalation. XRD results confirm this observation.

Materials produced by ion-exchange were shown to have the composition $Na_{0.2}Li_{0.24}MnO_2$ from the elemental analysis.. The open circuit voltage of lithium cells containing this material in the cathode was approximately 3.2 V before passage of current. After charging to 3.7 V, the discharge characteristics were nearly identical to those of cells containing chemically produced $Na_{0.2}MnO_2$, but slightly higher utilization was obtained at current densities above 0.1 mA/cm^2. In either case, better performances in lithium cells were obtained when $LiN(CF_3SO_2)_2$ was used as the electrolyte salt. The galvanostatic discharges shown in Figure 1b are for cells containing the ion-exchanged material in the cathode and $LiN(CF_3SO_2)_2$ as the electrolyte salt.

The depth of discharge decreased as current was increased beyond 0.1 mA/cm^2 for both the sodium and the lithium cases. This most likely reflects the limitations of the cathode active material, as other intercalation electrodes such as Na_xCoO_2 can be fully utilized at up to 0.5 mA/cm^2 in the same cell configuration[10].

Li/PEO/$Na_{0.2}MnO_2$ and Li/PEO/$Na_{0.2}Li_{0.24}MnO_2$ cells exhibited large overpotentials in the latter portion of the discharges at low rates, even when the current was interrupted for several hours at various intervals. While the OCV profile is relatively featureless, the discharge curves are sigmoidal, reflecting the increased overpotential. Na_xMnO_2 contains several types of sites potentially available for ion insertion; one type in the smaller irregularly shaped tunnels and four sites of two types of symmetry in the large S-shaped tunnels. It is likely that the 0.2 Na/Mn present in the fully charged material is located in the smaller tunnels and that the increased resistance to lithium insertion in the nearly fully lithiated material is due to inter-ion repulsion in the large tunnels. This behavior

is not seen in $Na/PEO/Na_xMnO_2$ cells, which exhibit a slightly lower capacity for ion insertion. This implies that fewer sodium ions can be inserted into the large tunnels because of their greater ionic size. The position of the intercalated ions in the tunnels is clearly relevant to the performance characteristics of the batteries, and requires further study. A more complete structural analysis is currently underway in this laboratory.

Three types of cells with sodium manganese oxide electrodes were cycled continuously at 0.1 mA/cm^2 (Figure 2). For cells with sodium anodes and PEO separators, utilization dropped to less than 50% by the sixtieth cycle. The x-ray diffraction patterns on cycled and uncycled cathodes were identical, ruling out structural changes as an explanation for the loss of capacity. Even greater capacity fading was seen in the second type of cell with two Na_xMnO_2 electrodes and a PEO separator, in which sodium ions were cycled back and forth between the two manganese oxide electrodes. It is significant that loss of capacity occurs even in the absence of metallic sodium, and indicates that corrosion at the Na/PEO interface is not responsible for the deterioration in performance of the first type of cell. This phenomenon must therefore be attributed to changes in the other components or interfaces upon cycling.

Figure 2 also shows a $Li/P(EO)_8LiN(CF_3SO_2)_2/Na_{0.2}Li_xMnO_2$ cell that was charged and discharged 93 times at 0.1 mA/cm^2. The voltage limits were varied throughout the discharge. While it is clear that the increase in voltage limits after the fortieth cycle resulted in over-extraction and over-insertion of ions and eventually led to deterioration of performance, capacity retention is better than in the sodium case. Again, no evidence of phase change upon cycling was seen for

this system. This in itself is remarkable, as many manganese oxides undergo a conversion to a spinel structure upon cycling in lithium cells[11].

Some deterioration of performance is almost always seen in alkali metal/polymer batteries with metal oxide cathodes and is sometimes severe[10]. The causes for this are not well-known, and are apt to be very system-specific. Koksbang et al[12] have suggested that increasing interparticle resistance and disconnection in the cathode induced by the volume changes occurring during intercalation/de-intercalation is responsible for loss of capacity in lithium/polymer cells with V_6O_{13} electrodes. Intercalation of sodium ions into Na_xMnO_2 is expected to cause a larger volume change than intercalation of lithium; this might explain the differences in cycling behavior between the $Li/PEO/Na_{0.2}Li_xMnO_2$ and the $Na/PEO/Na_xMnO_2$ cells seen in this study. Capacity fading may also be caused by slow oxidation of the electrolyte by the fully charged manganese oxide, corrosion at the current collector interfaces, and/or mass transfer effects. These phenomena can easily be minimized by lowering the voltage limit upon charge, improving electrolyte compositions and current collector materials and by judicious use of rest periods between half-cycles. At any rate, these early results demonstrate that the orthorhombic sodium manganese oxide is remarkably stable and undergoes alkali metal intercalation processes readily and reversibly.

Conclusions

The suitability of the orthorhombic sodium manganese oxide for use as a cathode material in alkali metal secondary batteries has been demonstrated. This material, which has never before been used in a battery, has high specific capacity in both lithium and sodium cells, and discharge characteristics suitable for use with polymer electrolytes. An especially striking feature is the excellent reversibility and stability upon cycling in lithium cells.

Acknowledgment

Figure Captions

1 a)   Continuous galvanostatic discharges at various current densities for $Na/P(EO)_8NaCF_3SO_3/Na_xMnO_2$ cells at 85° C. The cathodes contained $Na_{0.44}MnO_2$ and were charged initially. (■) denotes OCV readings for $Na/P(EO)_8NaCF_3SO_3/Na_xMnO_2$ cells. Some OCV readings were taken from cells with chemically produced $Na_{0.2}MnO_2$ in the cathodes (see text). 1b) Continuous galvanostatic discharges at various current densities for $Li/P(EO)_8LiN(CF_3SO_2)_2/Na_{0.2}Li_xMnO_2$ cells at 105° C. The lithium ion-exchanged material was used in the cathodes and the cells were charged initially. (■) denotes OCV readings for $Li/P(EO)_8LiCF_3SO_3/Na_{0.2}Li_xMnO_2$ cells at this temperature. Chemically produced $Na_{0.2}MnO_2$ was used in the cathodes for the OCV readings.

2). Capacity as a function of cycle number for cells continuously discharged and charged at 0.1 mA/cm^2. (■) $Li/P(EO)_8LiN(CF_3SO_2)_2/Na_{0.2}Li_xMnO_2$ at 105° C. Voltage limits were varied for this case. (x) $Na/P(EO)_8NaCF_3SO_3/Na_xMnO_2$ at 85° C. (Δ) $Na_xMnO_2/P(EO)_8NaCF_3SO_3/Na_xMnO_2$ at 85° C.

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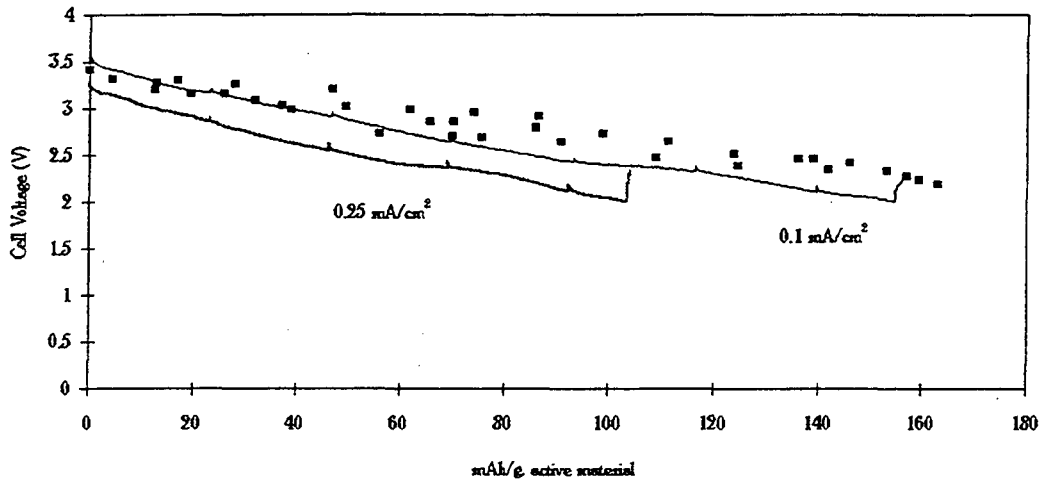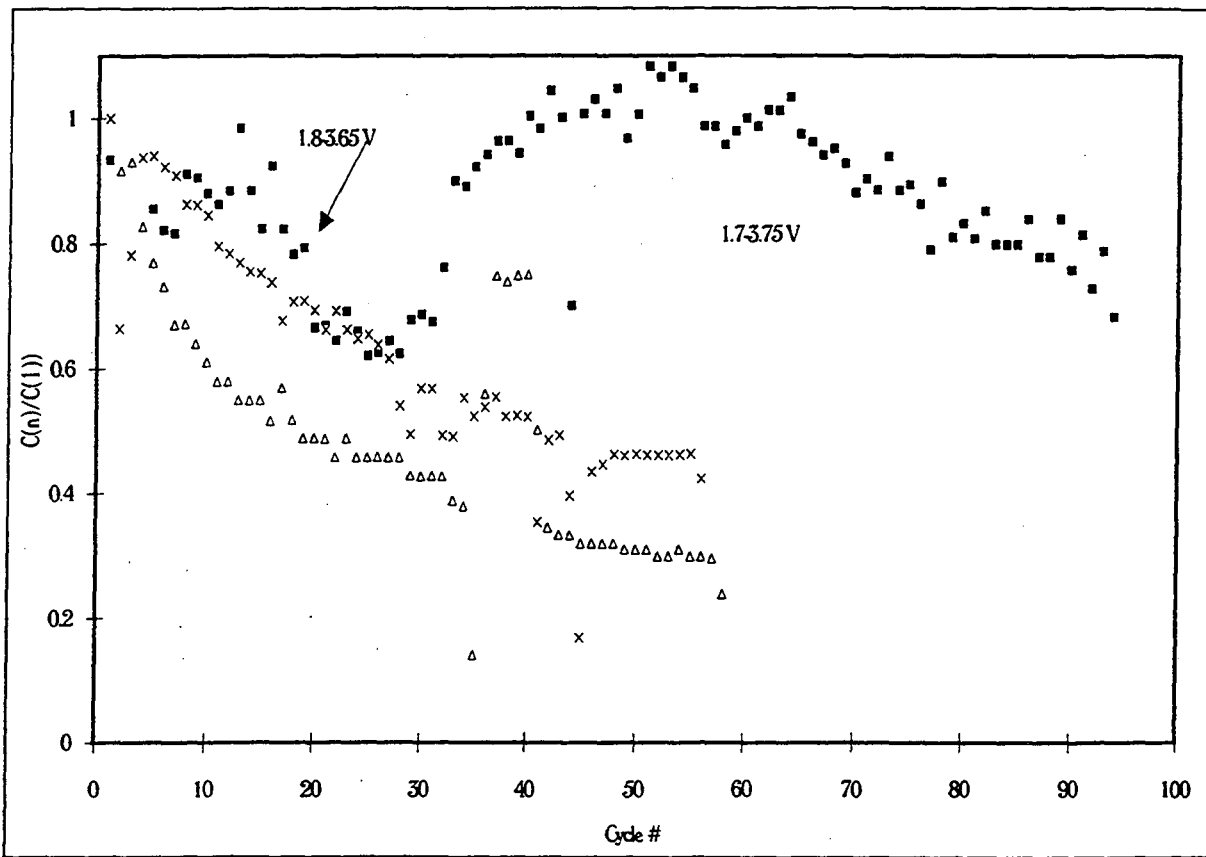
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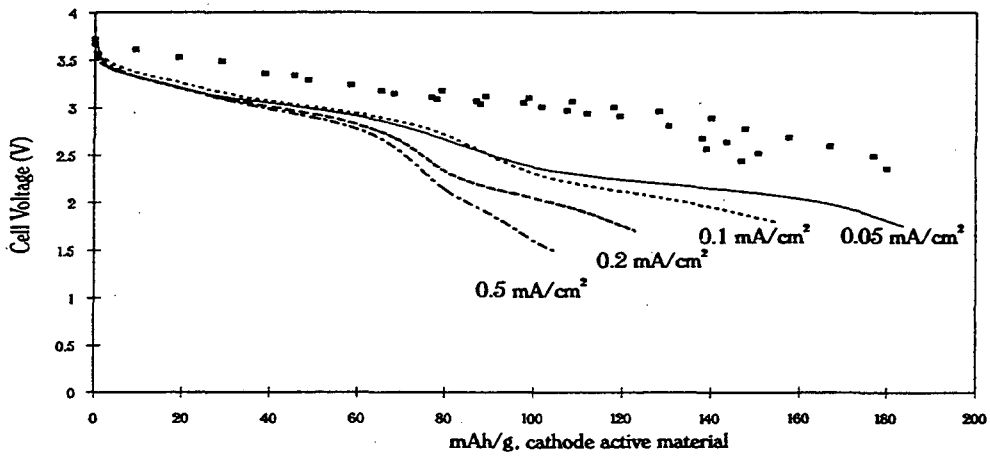
(b)

Figure 1

Figure 2

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