Lithium Potassium Manganese Mixed Metal Oxide Material for Rechargeable Electrochemical Cells

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ABSTRACT

A family of potassium-doped manganese oxide materials were synthesized with the stoichiometric formula $Li_{0.9-x}K_xMn_2O_4$, where $X = 0.0$ to 0.25, and evaluated for their viability as a cathode material for a rechargeable lithium battery. A performance maximum was found at $X = 0.1$ where the initial specific capacity for the lithium - potassium doped manganese dioxide electrochemical couple was 130 mAhrs/g of active cathode material.

INTRODUCTION

Manganese dioxide doped with potassium was examined as a cathode material for rechargeable lithium and lithium-ion batteries. The goal of this effort was to provide a new mixed metal oxide cathode material for use as the positive electrode in rechargeable lithium and lithium ion electrochemical cells. A stable mixed metal oxide was fabricated by doping manganese dioxide with potassium. This material was then used as an intermediate for further processing and lithiation for use in rechargeable lithium batteries. [1-3]

Electrochemical measurements were performed on rechargeable lithium batteries using potassium-doped manganese dioxide as the positive electrode. The changes in cell behavior as a function of potassium stoichiometry in MnO_2 were evaluated. Optimization of cell discharge and charge properties with respect to the potassium and lithium stoichiometry was a goal during these measurements. Additional research was focused on the characterization of the $Li_{0.9-x}K_xMn_2O_4$ material and the stability of cell components. For comparison $Li//Li_{0.9}Mn_2O_4$ electrochemical cells were fabricated and evaluated in parallel with the $Li//Li_{0.9-x}K_xMn_2O_4$ electrochemical cells.

EXPERIMENTAL

The $Li_{0.9-x}K_xMn_2O_4$ material used in this study was prepared through a series of solid-state reactions. Mixing KOH and MnO_2 and heating in an annealing oven for 72 hours resulting in $K_xMn_2O_4$. The material was further processed forming $Li_{0.9-x}K_xMn_2O_4$ by mixing LiOH and $K_xMn_2O_4$ and heating in an annealing oven for 72 hours. After preparation, the materials were characterized with X-ray diffraction and stored in argon filled dry box.

In addition to KOH and LiOH, K_2CO_3, K_2O and Li_2CO_3, Li_2O_2 and Li_2O were used during the synthesis process. The $Li_{0.9-x}K_xMn_2O_4$ preparation also included other manganese oxides (Mn_2O_3 and Mn_3O_4) in addition to MnO_2 as the starting material. Synthesis with the variant starting materials yielded similar product. X-ray diffraction was used to analyze both the intermediate and final product after the heat treatment step. The heat treatment was repeated whenever incomplete conversion was indicated by the X-ray diffraction pattern.

After mixing the reactants for the potassium doped intermediate and the final lithiated product, the materials were heated to 900^oC in air. The heat treatment involved an approximately 15 minutes to 90% heating cycle, a 72 hours soak time, followed by a two step cool down; 4 hrs to 300^oC then quenching to 20^oC. A modified heating regiment, where the raw materials heated for 16 hrs at 450^oC and remixed prior to the 900^oC cycle, improved the homogeneity of the product.

Initial stoichiometry included $X = 0.0$, 0.05, 0.1, 0.15, 0.2 and 0.25 in $Li_{0.9-x}K_xMn_2O_4$. Subsequent stoichiometry included $X = 0.025$, 0.075, and 0.125 in order to complete the performance matrix and 0.1, 0.15 and 0.2 stoichiometry to verify reproducibility of previous results.

Test cells were fabricated in order to evaluate the electrochemical properties of the lithium/potassium doped manganese dioxide electrochemical system. Experimental Teflon button cells were used in the evaluation. The button cell consisted of two Teflon plates with 1.9 cm diameter cylindrical recesses machined into each plate. The bottom of the recess had a small through hole for wire connection to the electrode. A nickel, stainless steel or platinum electrode current collector was set into the bottom of the recess. The sections of the test fixture were secured together with screws, alloying for postmortem analysis of the cell components. The cell was placed in a reaction vessel and electrolyte was backfilled into the vessel completely covering both electrodes. Additional electrochemical evaluation was conducted using conventional button cells of similar dimension to the Teflon cell.

The experimental cells were composed of a lithium anode separated from a Teflon bonded cathode with a nonwoven glass separator. The cathode was fabricated by mixing together $Li_{0.9-x}K_xMn_2O_4$, carbon and Teflon in a 6:3:1 by weight ratio respectively. The cathode mix was rolled to 0.04 cm and dried in a vacuum oven. 0.075 cm thick lithium foil was cut using a 1.75 cm diameter (2.48 cm^2) hole punch. The cathode was also cut to 2.48 cm^2, resulting in a 0.1 g to 0.12 g

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14. ABSTRACT

A family of potassium-doped manganese oxide materials were synthesized with the stoichiometric formula $Li_{0.9-x}K_xMn_2O_4$, where X = 0.0 to 0.25, and evaluated for their viability as a cathode material for a rechargeable lithium battery. A performance maximum was found at X = 0.1 where the initial specific capacity for the lithium - potassium doped manganese dioxide electrochemical couple was 130 mAhrs/g of active cathode material.

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cathode. A 0.01 cm nonwoven glass separator was utilized for the separator and as a wick. The electrolyte used was 1 molar $LiPF_6$ in proportional mixtures of diethyl carbonate, dimethyl carbonate and ethylene carbonate.

The cells were cycled with an ARBIN Model BT-2043 Battery Test System. A two-step charge profile was used. The charge profile consisted of a constant current charged at 1.25 mA (0.5 mA/cm^2) or 2.5 mA (1 mA/cm^2) to 4.3 volts followed by an applied constant voltage of 4.3 volts. The constant voltage was maintained for 5 hours or until the charge current dropped to 0.1 mA. Typically the constant voltage portion of the charge was maintained for less than 1 hour before reaching the 0.1 mA cutoff current. The cells were discharged at 1.25 or 2.5 mA to 2.5 volts. A rest period of 15 minutes between charge and discharge cycles allowed for the cells to achieve equilibrium. The 1.25 mA profile yielded an approximately 10 hour cycle time. The 2.5 mA cycle was used to speed up the cycle life study.

RESULTS
Figure 1 shows the X-ray diffraction patterns for $Li_{0.8}K_{0.2}Mn_2O_4$, $Li_{0.8}K_{0.1}Mn_2O_4$, and $Li_{0.9}Mn_2O_4$ cathode materials. Included in the figure is the 35-0782 $LiMn_2O_4$ X-ray diffraction card file. The X-ray patterns show additional diffraction angle peaks present in the potassium-doped material. It should be noted that while most of the peaks have similar magnitudes, including the additional peaks there are notable exceptions. The peak at $28.5°$ 2Θ increases with increased potassium content and the peak at $65.5°$ 2Θ decreases with increasing potassium content. These X-ray patters are representative of the materials used in the cells fabricated for this paper.

Figure 2 shows comparative discharge curves for cathode material with "X" in $Li_{0.9-x}K_xMn_2O_4$ equal to 0.0, 0.1 and 0.2. The data in Figure 2 shows the 10th discharge for each cell and are typical discharges for each stoichiometry. The cells for this experiment were charged and discharged at 0.5 mA/cm^2, which resulted in a 12 to 14 hour discharge. The data shows the enhanced discharge capability of cells with a $Li_{0.8}K_{0.1}Mn_2O_4$ cathode. The data also shows a detrimental result for cells with a $Li_{0.7}K_{0.2}Mn_2O_4$ cathode. The data also clearly shows the two thermodynamic plateaus in the discharge curve indicating a phase change with lithium insertion into the cathode. Figure 3 displays graphically the capacity obtained during discharge of the two thermodynamic plateaus. The plot shows an initial decrease in capacity delivered during the first thermodynamic plateau (> 3.5 volts). This initial decrease is followed by a maximum in capacity delivered as X approaches 0.1 then a steady decrease in capacity delivered as X increases greater than 0.1. The data also shows an increase in the 2.5 Volt plateau as X increases from 0.0 to 0.25.

Figure 4 shows the 10th & 11th charge/discharge Curve for a $Li//Li_{0.8}K_{0.1}Mn_2O_4$ cell. The cell for this experiment was charged and discharged at 0.5 mA/cm^2 after 2 days of casual storage. The data shows a coulombic overcharge of 0.218 mAhr for the 10th charge cycle followed by a 0.058 mAhr overcharge for the 11th charge. This corresponds to coulombic efficiencies of 97 and 99 percent. The data also shows the low overpotential required for charge, resulting in a 93 and 95 percent energy efficient charge for the 10th and 11th cycle, respectively. This data also clearly shows the two thermodynamic plateaus for the $Li//Li_{0.9}Mn_2O_4$ electrochemical system. Additional investigation reveals a slight two-stage division of the greater than 3.5 volt thermodynamic plateau.

Figure 5 shows the capacity in mA-hr/gram of active cathode material for various stoichiometry of potassium in the $Li_{0.9-x}K_xMn_2O_4$ material. The graph displays the capacity at the 10th cycle and 100th cycle. The discharge profile for this series of tests was 0.5 mA/cm^2 through 25 cycles then 1.0 mA/cm^2 charge-discharge profile for 23 cycles followed by two cycles at 0.5 mA/cm^2. The loss of capacity between the 75th and 100th cycle was due to the reduction and final elimination of the 2.5 volt plateau. Figure 6 shows the discharge data set for the case where the stoichiometry of potassium in $Li_{0.9-x}K_xMn_2O_4$ is $X = 0.15$. This data shows a rapid decrease in capacity during the 76th to 98th, 1.0 mA/cm^2 cycles. Figure 7 shows the data for the case where the stoichiometry of potassium in $Li_{0.9-x}K_xMn_2O_4$ is $X = 0.125$. Two cells from the same lot were discharged at 1.0 mA/cm^2 however the cut off voltage were set at 2.5 and 3.0 volts. This test was designed to show the performance of the cell if the lower voltage plateau is not used during discharge.

DISCUSSION
The data presented here shows the discharge characteristics of a family of potassium-doped lithium-manganese oxide materials. This material with the stoichiometric formula $Li_{0.9-x}K_xMn_2O_4$ where $X = 0.0$ to 0.25 proved to produce a viable reversible electrochemical couple with lithium. The material demonstrated a performance maximum when $X = 0.1$, where the initial specific capacity for the lithium - potassium doped manganese dioxide electrochemical couple was 130 mAhrs/g of active cathode material. The discharge capacity of the system was maintained through 90 cycles (95 percent of initial capacity). Additionally, the capacity was maintained at a level greater than 90 percent of initial discharge capacity through 200 cycles.

Table 1 compares the capacity of the synthesized potassium doped lithium-manganese dioxide material with the stoichiometric formula $Li_{0.9-x}K_xMn_2O_4$ where $X = 0.0$ to 0.25 to the theoretical capacity of the material. Two values for the theoretical capacity are shown in the table: one representing a 1.0 valence change and the other $1.0 - X$ representing the stoichiometry of lithium in the reaction. A 3-volt discharge termination is used since it is consistent with the application of the chemistry. Additionally a 3-volt cut-off represents the sustainable capacity of the system. The capacity obtained at a

2.5-volt cut-off was maintained through the initial discharges with degradation of the lower thermodynamic plateau after 90 cycles.

In addition, the data shows that synthesized potassium doped lithium manganese oxide material with stoichiometry around the X = 0.1 maximum have comparable performance. These materials had an initial specific capacity in the order of 130 mAhr/g, and maintained a capacity of 115 mAhr/g for over 25 cycles. The capacity of the system was maintained at 90 percent of the initial capacity through 90 cycles. After 90 cycles a low voltage thermodynamic plateau degrades resulting in a capacity that

is 75 percent of the initial capacity. The final failure of the cell was typically due to lithium dendrites formed during charge. These dendrites form after 200 cycles and were not unexpected due to the cell design, in particular the open separator used.

REFERECES

1) Terrill B. Atwater and Alvin J. Salkind, US Patent No. 6,770,398, 3 Aug. 2004
2) Terrill B. Atwater and Alvin J. Salkind, US Patent No. 6,982,048, 3 Jan. 2006
3) Terrill B. Atwater and Alvin J. Salkind, *J. Power Sources*, In Course of Publication.

Table 1: Performance Characteristics of $Li_{0.9-x}K_xMn_2O_4$

Stoichiometry in $Li_{0.9-x}K_xMn_2O_4$	Chemical Formula	Molecular Weight	Theoretical Capacity (mAhr/g) $n = 1 - X$ (n = 1)	Capacity Delivered to 3.0 V	Percent Theoretical $n = 1 - X$ (n = 1)
X = 0.0	$Li_{0.9}Mn_2O_4$	180.12	149 (149)	111	74.6 (74.6)
X = 0.025	$Li_{0.875}K_{0.025}Mn_2O_4$	180.93	144 (148)	104	72.0 (70.2)
X = 0.05	$Li_{0.85}K_{0.05}Mn_2O_4$	181.73	140 (147)	105	74.9 (71.2)
X = 0.075	$Li_{0.825}K_{0.075}Mn_2O_4$	182.54	136 (147)	114	83.9 (77.6)
X = 0.10	$Li_{0.8}K_{0.1}Mn_2O_4$	183.34	132 (146)	117	88.9 (80.0)
X = 0.125	$Li_{0.775}K_{0.125}Mn_2O_4$	184.15	127 (146)	109	85.6 (74.9)
X = 0.15	$Li_{0.75}K_{0.15}Mn_2O_4$	184.95	123 (145)	95	77.1 (65.6)
X = 0.20	$Li_{0.7}K_{0.2}Mn_2O_4$	186.56	115 (144)	72	62.7 (50.1)
X = 0.25	$Li_{0.65}K_{0.25}Mn_2O_4$	188.17	107 (142)	38	35.6 (26.7)
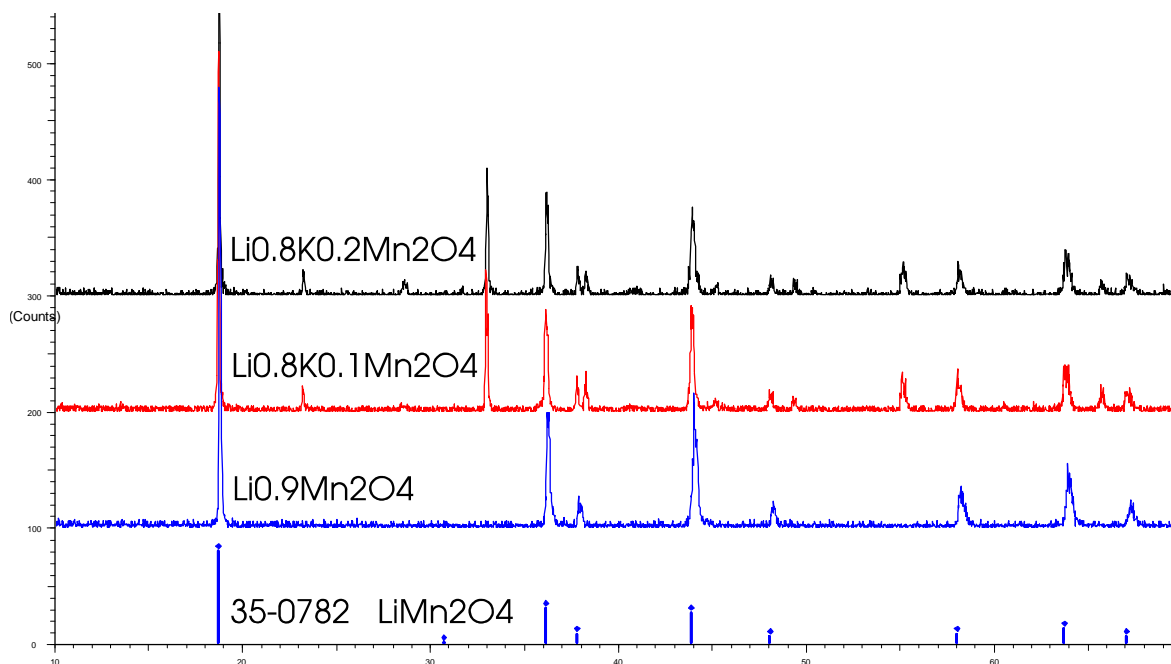
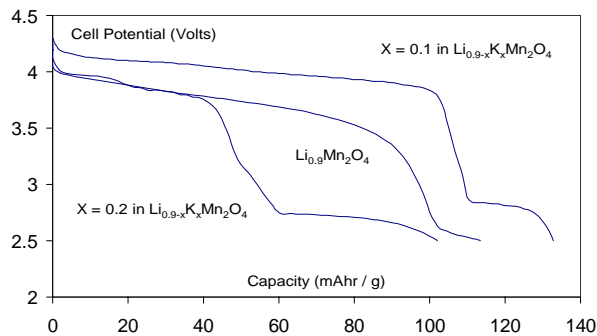Figure 1: X-ray diffraction patterns for $Li_{0.8}K_{0.2}Mn_2O_4$, $Li_{0.8}K_{0.1}Mn_2O_4$, and $Li_{0.9}Mn_2O_4$ cathode material

Figure 2: Comparative discharge curves with "X" in $Li_{0.9-x}K_xMn_2O_4$ equal to 0.0, 0.1 and 0.2.
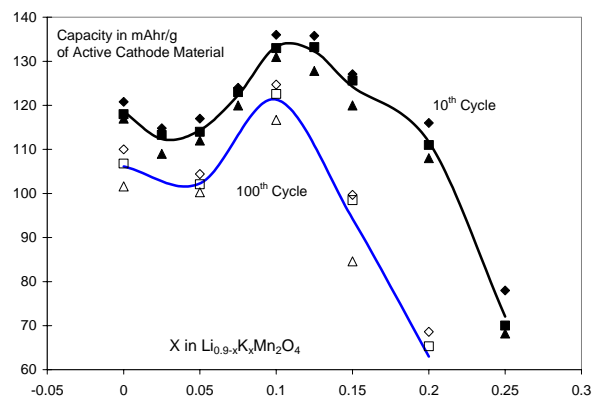

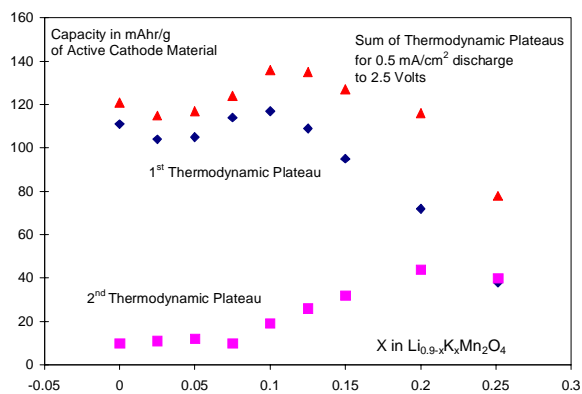Figure 5: Capacity delivered at the 10th cycle and 100th cycle for $Li_{0.9-x}K_xMn_2O_4$ material.

Figure 3: Capacity obtained during discharge for $Li_{0.9-x}K_xMn_2O_4$ cathode material. Two thermodynamic plateaus (>3.0 Volts and <3.0 Volts) displayed.
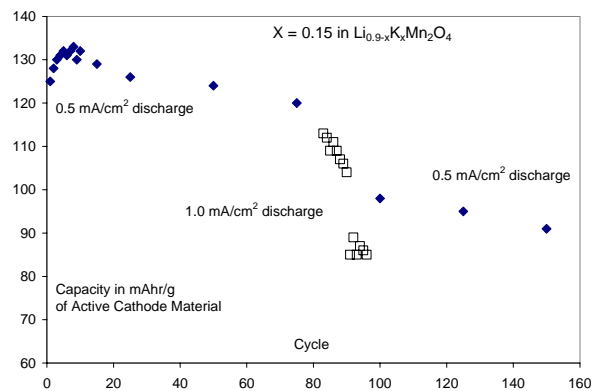

Figure 6: Discharge data set for $Li_{0.9-x}K_xMn_2O_4$ where X= 0.15.

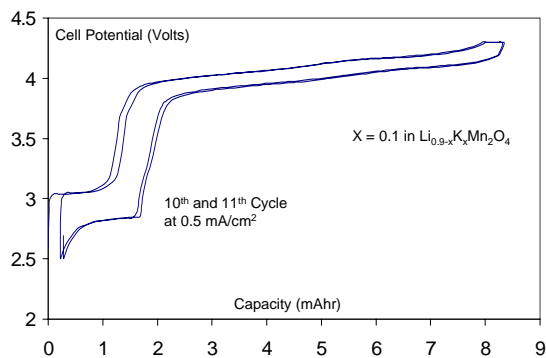Figure 4: Charge/discharge curve for 10th & 11th cycle for a $Li//Li_{0.8}K_{0.1}Mn_2O_4$ cell.
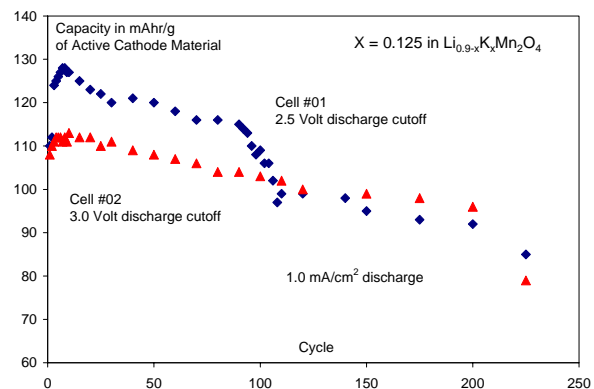

Figure 7: Data for X= 0.125.stoichiometry of potassium in $Li_{0.9-x}K_xMn_2O_4$
Cells discharged at 1.0 mA/cm^2
With the cut off voltage set at 2.5 and 3.0 volts.