

Halogenated Lithium Manganese Oxide $AB_2O_{4-d}X_d$ Spinel Cathode Material

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ABSTRACT

The benefits of lithium battery systems lie within their high energy density (Wh/L) and high specific energy (Wh/kg). Manganese dioxide (MnO_2) is an attractive active cathode material because of its high energy density and low material cost. Manganese dioxide is an intercalating compound for lithium that functions by solvating and desolvating lithium cations from the electrolyte in solid state. The lithium cations are deposited into the vacancies of the MnO_2 cathode crystal structure. The objective of this effort focuses on the limited cycle life of rechargeable lithium manganese-based electrochemical systems, most importantly capacity fading of the cathode. These two characteristics are considered the major technology hurdles in rechargeable lithium battery technology.^{1, 2, 3, 4}

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INTRODUCTION

A family of lithium manganese $AB_2O_{4-d}X_d$ materials was synthesized using a solid state reaction and evaluated as a cathode for lithium and lithium-ion electrochemical systems. The general formula for the material is $Li_xMn_2O_{4-d}X_d$ where $x \approx 1$ and d ranges from 0.005 to 0.3. By introducing halogens into the starting material mixture and subsequently into the final product, the synthesis process time of lithium manganese-based AB_2O_4 spinel materials is dramatically reduced. The material properties were verified with X-ray diffraction and X-ray fluorescence. Button cells were fabricated to evaluate the thermodynamic and kinetic properties of the $Li/Li_xMn_2O_{4-d}X_d$ electrochemical systems.

BACKGROUND

Capacity fading is the loss of cycle capacity in a cell over the entire life of a battery system, limiting the practical number of cycles that may be used. In lithium battery systems, capacity loss is often attributed to the degradation of the active cathode material. This degradation is a result of both changes in composition and crystal structure of the active material that occurs during both charging and discharging of the cell. The crystal structure of the active material changes in coordination with the state of charge of the cell. This is linked to intercalation of lithium cations into the active material. Additionally, throughout the life of a cell, parasitic side reactions occur between the chemical species of

the cell components. These include chemical dissolution and degradation of the active cathode material. Methods of reducing this effect include changing the crystal structure and composition of the active material or eliminating these parasitic mechanisms through other means. Capacity fading is currently a major setback for rechargeable lithium cells; therefore it is an active area of research.^{2, 3, 4, 5, 6, 7, 8, 9}

Manganese dioxide exists in different phase states or crystal structures. The common phases are referred to by the following prefixes: α , β , γ , and λ . α - MnO_2 is the most stable structure; it is a one-dimensional lattice containing both one-by-one and two-by-two channels for lithium insertion/extraction. γ - MnO_2 is a one-dimensional structure but has a one-by-two channel. λ - MnO_2 is created through the delithiation of Li-Mn-O type spinels ($Li_xMn_2O_4$). The crystal structure of the spinel is maintained through both delithiation and lithiation. The λ crystal structure is a three-dimensional cubic array. This structure promotes mechanical stability and adequate pathways for lithium insertion/extraction. λ - MnO_2 is perhaps the most preferred rechargeable phase of MnO_2 . Degradation of the λ - MnO_2 crystal structure forming α/γ - MnO_2 and other Mn_xO_y phases reduces the capacity of the cathode material.^{10, 11, 12, 13, 14, 15, 16, 17}

EXPERIMENTAL

A solid state process was used to fabricate the $\text{Li}_x\text{Mn}_2\text{O}_{4-d}\text{X}_d$ material where $x \approx 1$ and d ranges from 0.005 to 0.3 with MnO_2 or Mn_2O_3 , and Li_2CO_3 or LiOH as the principal starting material. Halogens are introduced into the starting material mixture and subsequent final product using lithium halide salts. These halide salts include lithium perchlorate (LiClO_4), lithium trifluoroacetate ($\text{LiC}_2\text{F}_3\text{O}_2$), and lithium trifluoromethanesulfonate (LiCF_3SO_3). The starting material mixture was ground using a random orbit mixer mill and was then heated in air at 600°C for a time period no greater than 4 hours. The material was evaluated for its viability as a cathode material for rechargeable lithium batteries.

The material properties were verified with X-ray diffraction and X-ray fluorescence. Button and laboratory glass test cells with a lithium anode and an organic electrolyte were fabricated to evaluate the thermodynamic and kinetic properties of the $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_{4-d}\text{X}_d$ electrochemical systems. The glass cell consisted of two machined pistons that are fitted into glass housings and secured with a threaded cap incorporating a pair of o-rings. The pistons, either aluminum, nickel, or stainless steel, had a surface area of 1.0 cm^2 . The pistons served as electrode current collectors and are threaded, allowing for an inert captivating ring to be employed to maintain electrode alignment. The glass fixture allows for postmortem analysis of the cell components. Conventional button cells with a surface area of 2.85 cm^2 were also used.

The experimental cells were composed of a lithium anode separated from the cathode by a nonwoven glass separator. The $\text{Li}_x\text{Mn}_2\text{O}_{4-d}\text{X}_d$ cathode was fabricated by mixing together the active material, carbon, and polytetrafluoroethylene with an 85:10:5 by weight ratio, respectively. The cathode mixture was rolled to 0.04 cm and dried in a vacuum oven. A 0.075 cm thick lithium foil was cut using a 12.7 mm or 19.0 mm diameter hole punch. The cathode was cut into 1.0 cm^2 and 2.85 cm^2 discs, resulting in a 0.05 g cathode for the glass cell and a 0.14 g cathode for the button cells. 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.

Cells were cycled with an ARBIN MSTAT4 battery cyclers system controlled by MITS Pro software. The charge/discharge rates were maintained at 0.5 to 4.0 mA/cm^2 , with the majority of electrochemical experiments cycled at 1.0 mA/cm^2 . The cells were charged to a cut-off of 4.75 to 5.0 V and discharged to a cut-off of 3.0 to 2.0 V . A rest period of 15 minutes between charge and discharge cycles was used to allow for cells to achieve equilibrium on all experiments.

RESULTS

After mixing and heating, the physical properties of the material were evaluated using powder X-ray diffraction, and the stoichiometry was verified using X-ray fluorescence. **Figure 1** shows the X-ray diffraction pattern for a family of $\text{Li}_x\text{Mn}_2\text{O}_{4-d}\text{Cl}_d$ where $x \approx 1$ and d ranges from 0.0 to 0.1 (bottom to top pattern). These patterns are representative of both the chlorinated and fluorinated $\text{AB}_2\text{O}_{4-d}\text{X}_d$ material. The undesirable Mn_2O_3 product was present in all samples. The Mn_2O_3 was minimal and appears to be controllable and possibly eliminated with refinement of the fabrication process. **Figure 2** shows an X-ray fluorescence pattern indicating the retention of Cl in the sample.

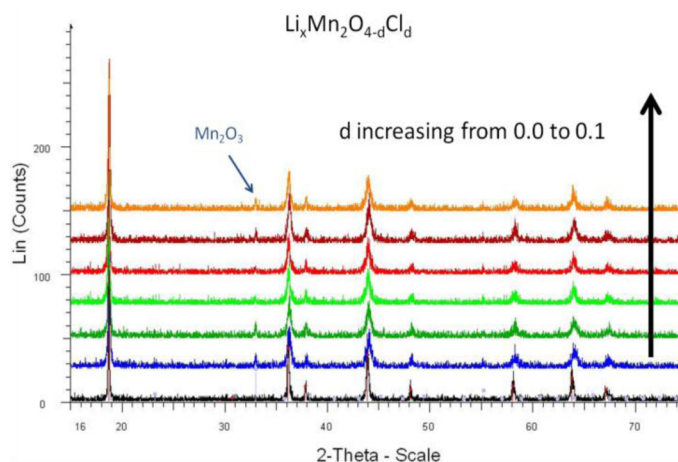


Figure 1. The X-ray diffraction pattern for a family of $\text{Li}_x\text{Mn}_2\text{O}_{4-d}\text{Cl}_d$ where $x \approx 1$ and d ranges from 0.0 to 0.1.

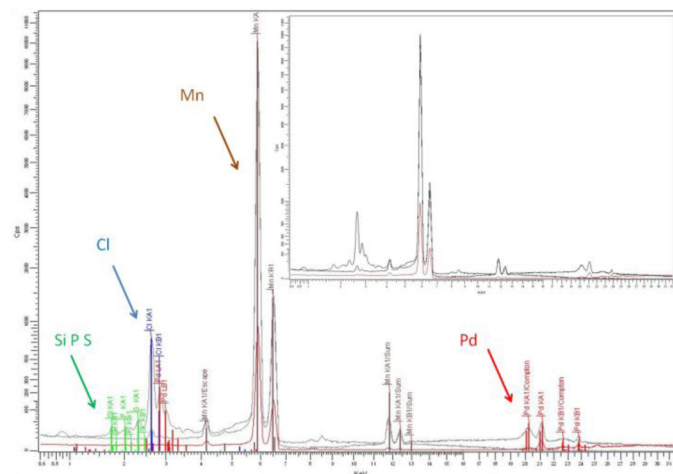


Figure 2. The X-ray fluorescence pattern indicating the presence of Cl in a $\text{Li}_x\text{Mn}_2\text{O}_{4-d}\text{Cl}_d$ sample.