

Comparison of the Entropy of Reaction in $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ Having Different Ratio of Li/Mn

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Introduction

The advantages of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ as an active cathode material in high power Li-ion cells are now well established.^{1, 2} The Li/Mn ratio in $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ must be carefully tuned^{3, 4} in order to trade off capacity and cycle life. During high current operation self-heating effects become important. Part of this heating is the reversible or entropic heating.

The entropy of reaction in LiMn_2O_4 has been measured by different groups.⁵⁻⁹ To the best of our knowledge, the effect of stoichiometry on entropy has not been studied. In this paper, the entropy of reaction in three spinel samples having different lithium contents $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($x = 0.03, 0.08, \text{ and } 0.14$) are compared as a function of state of charge.

Experimental

Three different Li-rich spinel samples $\text{Li}_{1.03}\text{Mn}_{1.97}\text{O}_4$, $\text{Li}_{1.08}\text{Mn}_{1.92}\text{O}_4$, and $\text{Li}_{1.14}\text{Mn}_{1.86}\text{O}_4$ were prepared by addition of Li_2CO_3 to stoichiometric spinel LiMn_2O_4 followed by baking in the presence of dry air flow. The chemical formula is the nominal composition based on the ratio of LiMn_2O_4 and Li_2CO_3 , and the Li to Mn ratios were further verified by Thermogravimetric analysis and X-ray diffraction. For each sample, 2325 type of coin cells were prepared using lithium foil as counter anode electrode, 1 M LiBF_4 in propylene carbonate/ethylene carbonate/diethyl carbonate (2/3/4) as the electrolyte.

The reaction entropy is proportional to dV/dT . There are two approaches for calculating dV/dT , 1) Measure constant current, full voltage curves at various temperatures, or 2) Hold the cell at each DOD, and ramp the temperature. Method one tends to result in large errors because the state of the cell changes from one cycle to the next. Method two suffers from self-discharge effects, but these effects can easily be subtracted out as will be described. In principle one can also extract reversible heating from calorimeter measurements, but this is very difficult because there is no way to simultaneously eliminate irreversible heating effects.

The coin cells were initially charged/discharged between 4.3 – 3V at $C_0/20$ for two cycles. The actual cell discharge capacity C was obtained based on the last discharge. SOC changes were carried out using a current corresponding to $C/20$. Cells were then equilibrated for 3 hours at $24 \pm 0.01^\circ\text{C}$ using a Lauda Circulator KS-6 in Paratherm NF bath liquid, connected to a MGW Lauda Digital Programmer PM-351. Open-circuit voltages (OCV) were recorded to within $\pm 0.001\text{mV}$ accuracy. After equilibration the temperature was ramped up to 30°C , and then back down to 24°C , at $0.1^\circ\text{C}/\text{min}$, all the while recording the OCV.

A linear relationship of temperature versus OCV can be obtained and the average of two slopes of increasing and decreasing temperature was considered as dV/dT at 100% of state of charge (SOC). The averaging

procedure removes self-discharge effects.

Results and Discussion

The dV/dT as a function of SOC for different spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($x = 0.03, 0.08, \text{ and } 0.14$) are plotted and compared in Figure 1.

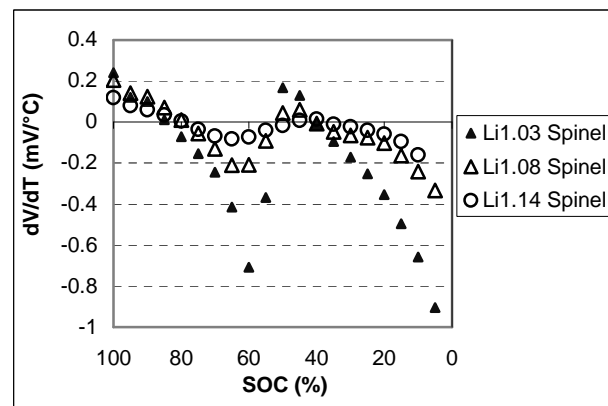


Figure 1. Entropy as a function of SOC

From these results we can make the following comments:

- $dV/dT > 0$ corresponds to an endothermic process on discharge.
- Numerous sign changes can be associated with Li ordering at 50%.
- The entropy tends toward zero for large x , presumably because the crystallinity of the material is decreasing.
- This is a general trend with technological significance. For example large exotherm at 0% SOC is responsible for the strong upturn in heating rate, commonly seen at the end of high current discharge.¹⁰
- For example: $dV/dT = -12.20, -1.61 \text{ mV}/^\circ\text{C}$ for $x = 0.03, \text{ and } 0.08$, respectively, at 0% SOC. These values were left off the graph for clarity.

Reversible heating results for some of the new layered mixed materials will also be presented.

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