

FOCUSED BATTERY TECHNOLOGY WORKSHOP III
 Material Challenges for High Energy Density and Long-life Lithium-Ion cells
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Title of Presentation (times new roman, 12, bold, centered)

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Introduction:

Please follow this template to make your abstract. Short abstract should be a **1 page, 2-column** document in Times New Roman, 10, single line spaced.

The rest of this text is a template to be used for your abstract.

$$\Delta S(x) = F \frac{\partial E_0(x, T)}{\partial T} \Big|_x$$

$$\Delta H(x) = F(-E_0(x, T) + T \frac{\partial E_0(x, T)}{\partial T} \Big|_x)$$

To minimize the effect of self-discharge during the temperature variation that may alter the electrode composition, temperatures lower than the ambient ones were used.

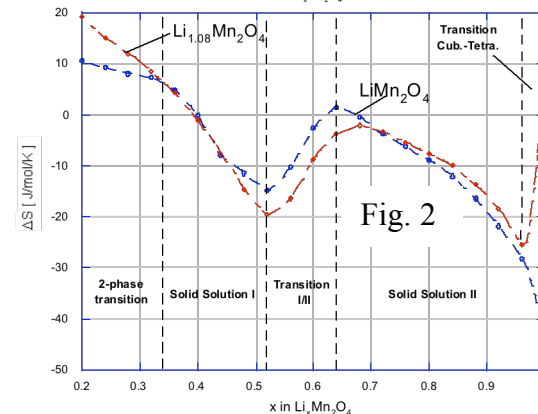
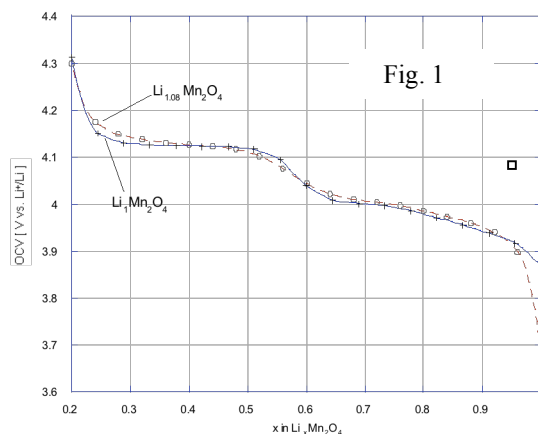
Experimental:

Aluminum coated cathodes based on stoichiometric $\text{Li}_1\text{Mn}_2\text{O}_4$ and lithium-rich $\text{Li}_{1.08}\text{Mn}_2\text{O}_4$ were provided by courtesy of ENAX Co., Japan. Half-cells consisting of 2016 coin-cells using metallic lithium as the counter and the reference electrode and 1M LiClO_4 in PC as electrolyte were prepared in an argon filled dry box and cycled galvanostatically (C/10 rate) between 2.9 and 4.4V for 5 cycles at the room temperature. This allows the charge and discharge capacity to stabilize. The thermodynamics data were then recorded using the ETMS as described in a previous work³.

Results:

Fig. 1 shows the OCV profile of the two cathodes taken at the room temperature. Both show typical two '4V' plateaus covering the 0.2-0.6 and 0.6-1.0 composition range. Differences in the profiles can be seen such as a flatter high voltage plateau in stoichiometric the stoichiometric material and a lower end tail (around $x=1$) in the non stoichiometric one. The corresponding entropy curves are displayed in Fig. 2 and were divided according to phase transitions at defined compositions. The entropy profiles are also different in both materials. In fact the two-phase system behavior is more pronounced in the stoichiometric material at low Li composition (up

to $x \sim 0.33$). A sharp increase in the non-stoichiometric material for $x > 0.95$ is also observed. Such differences may be due to stoichiometry related delays in phase transitions, in particular the cubic to tetragonal phase transition around $x=1$. Other phase transitions will be discussed in this presentation.



OCV (Fig.1) and entropy (Fig. 2) profiles of stoichiometric and non stoichiometric $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode materials.

References:

- ¹ K. E. Thomas et al. JECS 148(2001)A570
- ² Y. Reynier et al. J. Power Sources 119-121(2003)850
- ³ B. Fultz et al. Phys. Rev. B 70(2004)174304