

IN SITU XAS AND XRD STUDIES OF SUBSTITUTED SPINEL LITHIUM MANGANESE OXIDES IN THE 4-5 V REGION

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ABSTRACT

Partial substitution of Mn in lithium manganese oxide spinel materials by Cu and Ni greatly affects the electrochemistry and the phase behavior of the cathode. Substitution with either metal or with a combination of both shortens the 4.2 V plateau and results in higher voltage plateaus. *In situ* x-ray absorption (XAS) studies indicate that the higher voltage plateaus are related to redox processes on the substituents. *In situ* x-ray diffraction (XRD) on $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ shows single phase behavior during the charge and discharge process. Three phases are observed for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and two phases are observed in the case of $\text{LiNi}_{0.25}\text{Cu}_{0.25}\text{Mn}_{1.5}\text{O}_4$. The electrolyte stability is dependent on both the operating voltage and the cathode composition. Even though Ni substituted materials have lower voltages, the electrolyte is more stable in cells with the Cu substituted materials.

INTRODUCTION

The spinel LiMn_2O_4 is attractive as a cathode material because of its low cost. However, it exhibits unacceptably high capacity fade. Several researchers have stabilized operation on the 4.1 V plateau by substitution of a small fraction (~2.5%) of the manganese ions with other metal cations such as Mg, and Zn (1). More recently there have been reports of larger substitutions (up to 25%) of other metals such as Ni and Cu (2-3). With these large substitutions there is a decrease in the length of the 4.1 V plateau and new voltage plateaus appear at higher voltages. In the case of $\text{LiNi}_{0.5}\text{MnO}_4$ the 4.1 V plateau is eliminated and a new plateau appears at 4.7 V (2). $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has two voltage plateaus, one that slopes between 4.1 and 4.4 V and the other at 4.95 V. In these mixed cation oxides it is important to know the effect of the Mn substitution on the phase behavior during cycling. Also it is important to determine the nature of the charge compensation on the various voltage plateaus. This can be done using a combination *in situ* x-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS). XRD can provide information on the phase changes that occur in battery materials during the charge/discharge cycle. XAS gives information on the oxidation state of the probed element, and it can be used to follow changes on the oxidation state of the various cations during the charge/discharge cycle. This paper reports results on $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and $\text{LiNi}_{0.25}\text{Cu}_{0.25}\text{Mn}_{1.5}\text{O}_4$.

EXPERIMENTAL

Materials preparation

$\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and $\text{LiNi}_{0.25}\text{Cu}_{0.25}\text{Mn}_{1.5}\text{O}_4$ were prepared by a sol-gel method by dissolving stoichiometric amounts of the respective metal acetates in deionized water. The materials were precipitated by adding four times the molar equivalent of NH_4OH . The mixture was stirred with gentle heating for 4 h and then concentrated to dryness on a rotary evaporator. The dried precursors were fired at 750°C to yield the spinel.

In situ XRD and XAS

Cathodes were made by casting a mixture of the cathode material ($\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ or $\text{LiNi}_{0.25}\text{Cu}_{0.25}\text{Mn}_{1.5}\text{O}_4$), acetylene black conductive diluent and a binder (PVdF in a fugitive solvent) on to an aluminum foil sheet. Disc electrodes (2.82 cm^2) were punched from the sheet and were incorporated in the cell with a Celgard separator and a lithium foil anode. The electrolyte was 1 M LiPF_6 in solvent mixture of 1EC:3EMC.

Details of the spectroelectrochemical cell and the *in situ* XRD and XAS experiments are given elsewhere (4).

RESULTS AND DISCUSSION

$\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$

In situ XRD results indicated that the charge/discharge processes in $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ occurred in a single phase. The XAS showed that there was residual Mn(III) in the initial material. The Mn(III) was oxidized to Mn(IV) on the sloping voltage plateau between 3.8 and 4.4 V. On the upper plateau at 4.95 V there was no further oxidation of Mn. XAS at the Cu K edge indicated the oxidation of Cu(II) to Cu(III) on the upper plateau.

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

In situ XRD on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ showed the presence of three cubic phases during charge. XAS studies indicated that there was less residual Mn(III) in the starting material than in the case of $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$. There was no further oxidation of Mn on the upper plateau at 4.7-4.8 V. All of the charge compensation on this plateau occurred on the Ni.

$\text{LiNi}_{0.25}\text{Cu}_{0.25}\text{Mn}_{1.5}\text{O}_4$

Figure 1 shows a charging curve for $\text{LiNi}_{0.25}\text{Cu}_{0.25}\text{Mn}_{1.5}\text{O}_4$. The spikes in the curve indicate where charging was interrupted to take XAS spectra. There is a small sloping plateau at about 4.2 V. Most of the charging occurs at a voltage of about 4.8 V.

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Figure 2 shows XRD patterns obtained during the first charge. This and the lattice parameter plot, in Fig. 3, indicate the presence of two cubic phases. At the end of charge there were still two cubic phases, indicating incomplete charge. Disparities in the charge and discharge capacities indicated electrolyte decomposition. Even though the voltage in the cell with $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was higher there was much less electrolyte decomposition. Apparently, the presence of Ni catalyzes electrolyte decomposition. This is consistent with the lower thermal stability of cells with LiNiO_2 (5).

Figure 4 shows the Mn K edge XANES during charge. The inset shows the Mn oxidation state as a function of charge. The oxidation state was determined from the edge position at half the absorption height. A calibrated curve of edge position versus oxidation state was determined from XAS spectra on MnO , Mn_2O_3 and MnO_2 . The results indicate that the residual Mn(III) is oxidized to Mn(IV) during the first 25% of charge. Similar data are shown in Figs. 5 and 6 for the Ni and Cu K edges. The results indicate that at the beginning of charge both Ni and Cu exist in the divalent state. At the beginning of charge neither Ni nor Cu participate in the charge compensation process. However, after 25-30% of charge both Ni and Cu contribute to the charge compensation process. Ni(II) is oxidized to Ni(IV) and Cu(II) is oxidized to Cu(III). However, the oxidation of Cu(II) to Cu(III) is incomplete due to electrolyte decomposition. The two electron oxidation of the Ni, versus the one electron oxidation of Cu, accounts for the higher capacity of the Ni substituted materials.

CONCLUSION

Partial substitution of Mn in the lithium manganese oxide spinel materials by Cu and Ni greatly affects the electrochemistry and the phase behavior of the cathode. Substitution with either metal or with a combination of both shortens the 4.2 V plateau and results in higher voltage plateaus. The higher voltage plateaus are related to redox processes on the substituents. The electrolyte stability is dependent on both the operating voltage and the cathode composition. Even though Ni substituted materials have lower voltages, the electrolyte is more stable in cells with the Cu substituted materials. In searching for higher voltage cathodes it is important to develop improved electrolytes and cathodes that will not catalyze electrolyte decomposition.

The Cu substituted material is particularly stable on cycling. This is due to the stability of the electrolyte and the fact that the cycling process occurs in a single phase. The nickel substituted materials result in electrolyte decomposition and the formation of multiple phases and are less stable on cycling.

ACKNOWLEDGMENT

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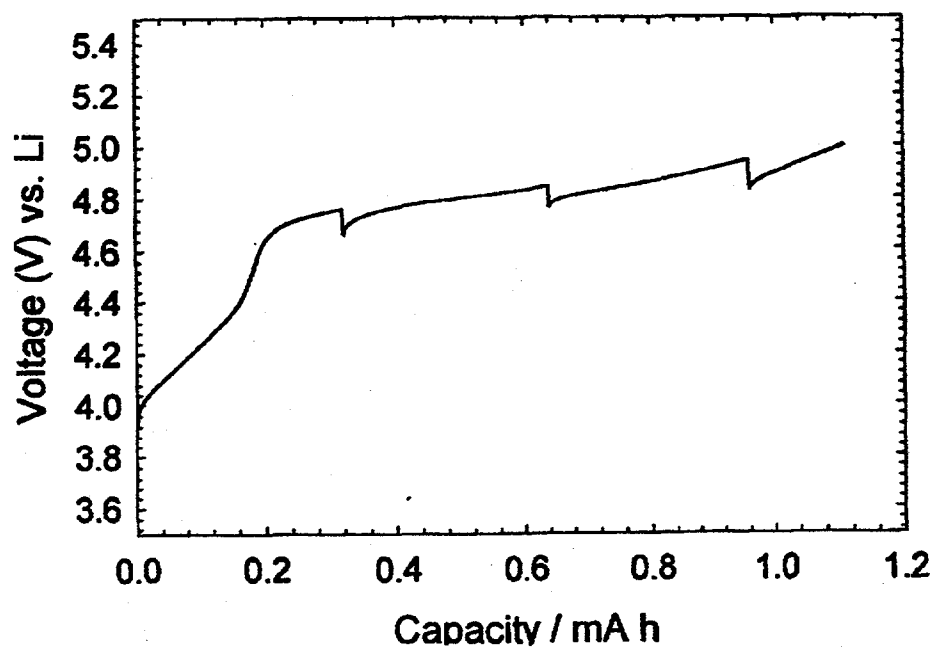


Fig. 1. Charging curve for $\text{LiNi}_{0.25}\text{Cu}_{0.25}\text{Mn}_{1.5}\text{O}_4$. The spikes indicate interruption of the charge to do XAS measurements at the Mn, Ni and Cu K edges.

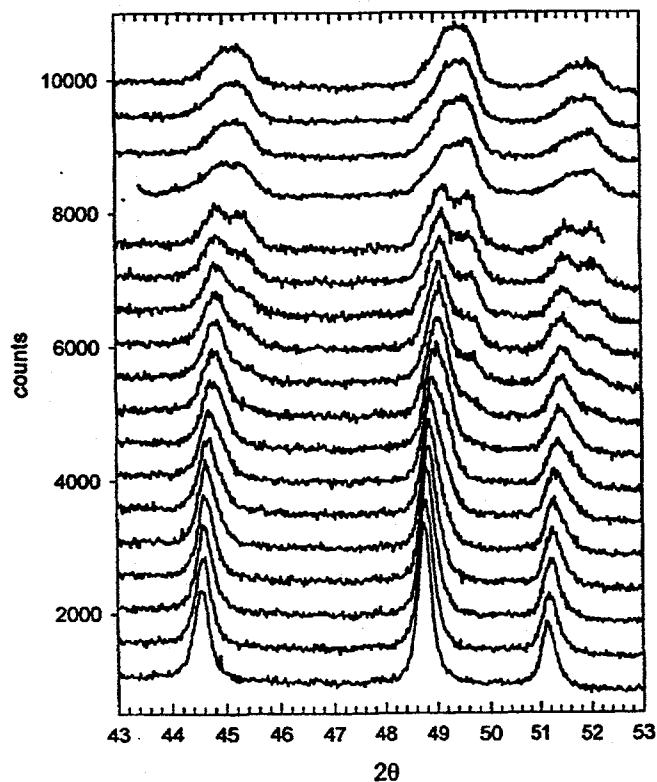


Fig. 2. XRD patterns during charge of $\text{LiNi}_{0.25}\text{Cu}_{0.25}\text{Mn}_{1.5}\text{O}_4$. Bottom, beginning of charge; top, end of charge.

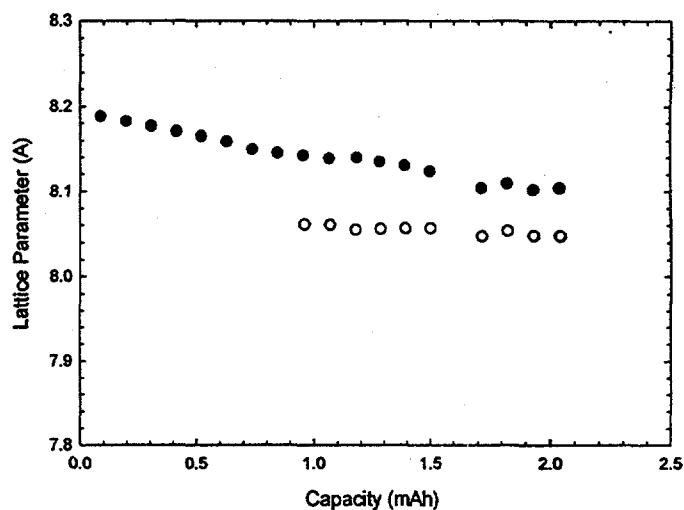


Fig. 3. Lattice parameters during charge of $\text{LiNi}_{0.25}\text{Cu}_{0.25}\text{Mn}_{1.5}\text{O}_4$.

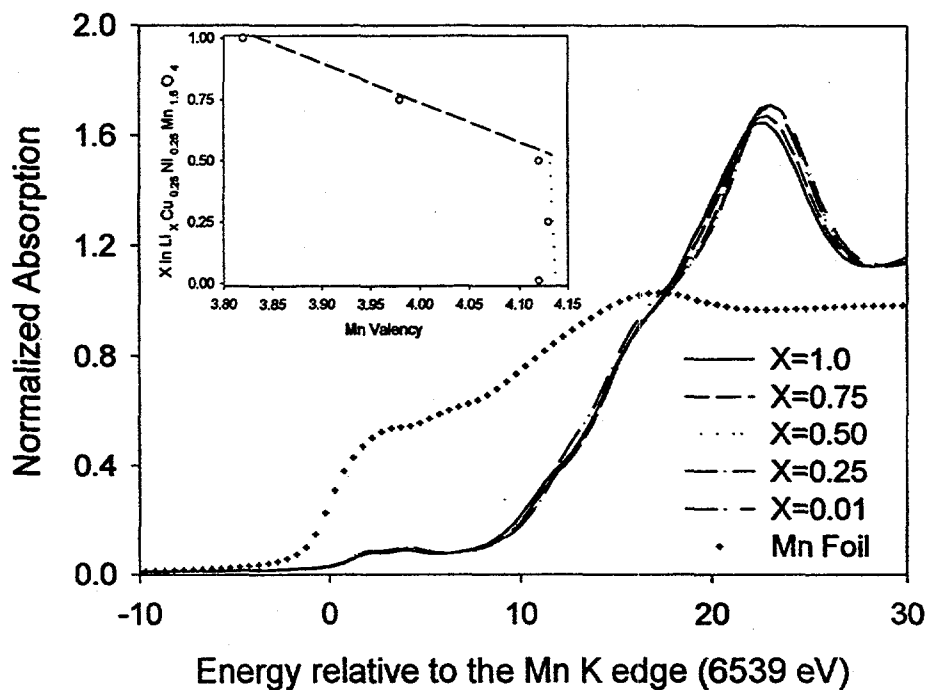


Fig. 4. Mn K edge XANES during charge of $\text{Li}_x\text{Ni}_{0.25}\text{Cu}_{0.25}\text{Mn}_{1.5}\text{O}_4$. Inset shows variation of Mn oxidation state with state of charge.

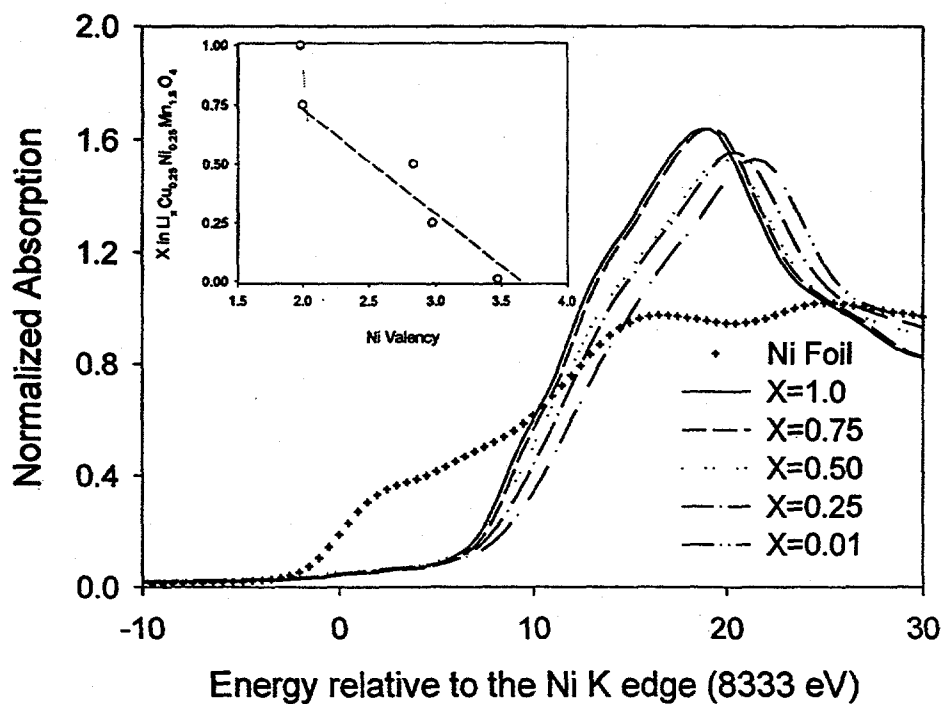


Fig. 5. Ni K edge XANES during charge of $\text{Li}_x\text{Ni}_{0.25}\text{Cu}_{0.25}\text{Mn}_{1.5}\text{O}_4$. Inset shows variation of Ni oxidation state with state of charge.

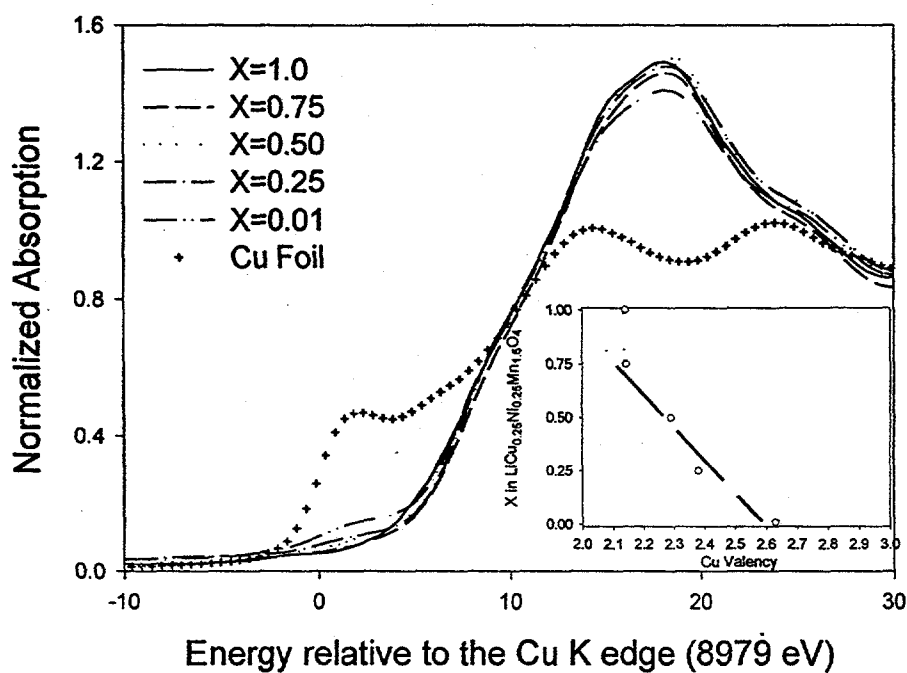


Fig. 6. Cu K edge XANES during charge of $\text{Li}_x\text{Ni}_{0.25}\text{Cu}_{0.25}\text{Mn}_{1.5}\text{O}_4$. Inset shows variation of Cu oxidation state with state of charge.