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Correlating Electronic Structure with Cycling Performance of Substituted LiMn_2O_4 Electrode Materials – A Study Using the Technique of Soft X-ray Emission

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INTRODUCTION

Rechargeable batteries based on LiMn_2O_4 cathodes have been suggested as an attractive alternative to the current nickel and cobalt based systems due to their relatively high energy density, low toxicity, and low cost [1]. Unfortunately, they exhibit a high degree of capacity fading [2]. Partial substitution of small quantities of metal cations for the Mn can significantly improve the cycling behavior of these electrode materials [2-6] – but at the expense of a decrease in initial capacity. For a given nominal oxidation state of Mn, data from W. Liu et al. [5] indicate that electrodes that have been substituted with Co cycle more efficiently than those that have been substituted with Ni. However, the relationship between the type and amount of metal substitution and the cycling enhancement has not been adequately explained.

L-edge x-ray emission spectroscopy (XES) of transition metals is a highly sensitive probe of covalency. As has been observed by these authors in Mn systems [7] and earlier by other groups studying Cu compounds [8], the higher the degree of covalency, the larger the ratio of L_α/L_β in transition metal complexes. In order to probe the covalency of these systems and to obtain a better understanding of the correlation between electrode performance and electrode composition, we have measured soft x-ray emission spectra on a series of $\text{LiMe}_y\text{Mn}_{2-y}\text{O}_4$ electrode materials (Me = Co, Ni, Li and $0 \leq y \leq 0.5$).

EXPERIMENTAL

Manganese L-emission spectra were recorded using the University of Tennessee soft x-ray fluorescence endstation on Beamline 8.0 at the Advanced Light Source [9]. A 925 l/mm grating was used to monochromatize the above threshold excitation energy for the emission measurements (Mn: ≥ 670 eV, Co: ≥ 825 eV, Ni: ≥ 900 eV) and a 1500 l/mm grating was used in the fluorescence spectrometer. With an entrance slit of 50 microns, the resolution of this detector corresponds to approximately 1.1 eV in the Mn fluorescence region. Mn Emission spectra were calibrated relative to the L_β emission of MnO [10] and the spectra were normalized to unit intensity at the L_β peak.

The LiMn_2O_4 and $\text{LiMe}_y\text{Mn}_{2-y}\text{O}_4$ (Me = Co, Ni, Li) samples were prepared as has been previously described [11] and the structures were confirmed by x-ray powder diffraction measurements. The dry powders were pressed into pellets for the XES measurements.

RESULTS AND DISCUSSION

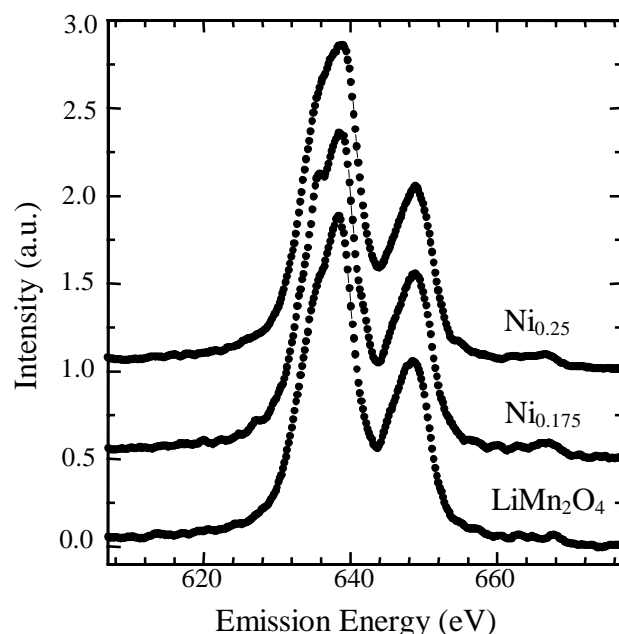


Figure 1. Mn L-emission Spectra of $\text{LiNi}_y\text{Mn}_{2-y}\text{O}_4$ Electrode Materials. Three different amounts of Ni-substitution ($y = 0.00, 0.175, 0.25$).

The L-edge XES spectra from a series of $\text{LiNi}_y\text{Mn}_{2-y}\text{O}_4$ electrode materials ($y = 0.00, 0.175, 0.25$) are presented in Figure 1. The L_α and L_β emission are centered here at 637.5 and 648.5 eV, respectively. Upon increasing the nominal Mn oxidation state by a higher level of Ni substitution, the intensity of the L_α peak (with respect to the intensity of the L_β peak) increases. The larger L_α/L_β ratio for the sample with a higher Mn oxidation state indicates an increase in the covalency of the Mn, as is expected. In order to correlate the dependence of this increase in covalency with the type of metal substitution, the spectra of a series of $\text{LiMe}_y\text{Mn}_{2-y}\text{O}_4$ electrode materials ($\text{Me} = \text{Co}, \text{Ni}, \text{Li}$) were simulated with four Lorentzian components.

The dependence of the relative covalence (the L_α/L_β ratio normalized to the L_α/L_β ratio of a sample of LiMn_2O_4 which was recorded under the same experimental conditions) on partial metal substitution of $\text{LiMe}_y\text{Mn}_{2-y}\text{O}_4$ electrode materials ($\text{Me} = \text{Co}, \text{Ni}, \text{Li}$) is shown in Figure 2. As the manganese oxidation state is increased by increased substitution with Co, the covalency of the Mn is increased. A similar trend is observed for Ni substitution. In addition, for a given average nominal Mn oxidation state, a sample substituted with Co is more covalent than one substituted with Ni which is in turn more covalent than a sample with Li-substitution.

This increase in covalency of $\text{LiMe}_y\text{Mn}_{2-y}\text{O}_4$ electrode materials with $\text{Me} = \text{Co}$ as compared to $\text{Me} = \text{Ni}$ mirrors the increase in cycling efficiency as seen by W. Liu et al. It is logical that greater covalency would be beneficial to electrode performance. The more covalent the Mn-O bond, the stronger the bond, making the spinel structure more resistant to the destructive expansion and contraction observed for LiMn_2O_4 electrodes.

As the cycling efficiency and covalency increase (for a given nominal Mn oxidation state), the crystal radius of the substituent is decreasing (effective crystal radius: $\text{Li}^+_{\text{oct}} = 0.90 \text{ \AA}$, $\text{Ni}^{2+}_{\text{oct}} = 0.83 \text{ \AA}$, $\text{Co}^{3+}_{\text{oct}} = 0.69 \text{ \AA}$ [12]) while the oxidation state of the substituent is increasing ($\text{Li}^+ < \text{Ni}^{2+} < \text{Co}^{3+}$). Further experiments with different types of metal substitutions will help to determine the driving force for the differences in covalency to allow further feedback for battery development.

We have shown that $\text{Mn } L_{\alpha}/L_{\beta}$ emission can be used to determine the relative covalency of potential $\text{LiMe}_y\text{Mn}_{2-y}\text{O}_4$ electrode materials. The positive correlation observed between covalency and cycling efficiency provides an explanation of improved cycling properties as a function of metal substitution and should allow identification of promising candidates for high performance rechargeable batteries with quick turnaround time.

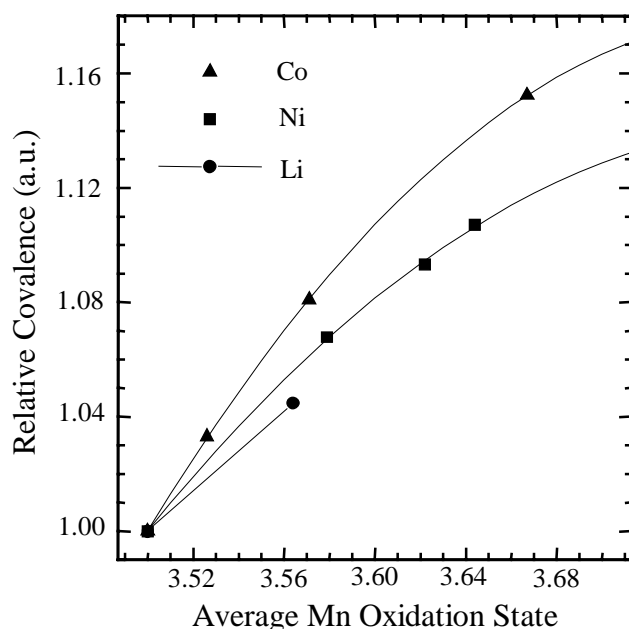


Figure 2. Dependence of the Relative Covalence of $\text{LiMe}_y\text{Mn}_{2-y}\text{O}_4$ Electrode Materials (Me = Co, Ni, Li and $0.00 \leq y \leq 0.25$) on the Nominal Mn Oxidation State.

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