

chemistry and structure

Changes in the local structure of $\text{LiMg}_y\text{Ni}_{0.5-y}\text{Mn}_{1.5}\text{O}_4$ electrode materials during Lithium extraction

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The effect of composition and preparation temperature on the structure of $\text{LiMg}_y\text{Ni}_{0.5-y}\text{Mn}_{1.5}\text{O}_4$ compounds were studied. For $y \geq 0.25$, cation ordering in a $\text{P4}_3\text{32}$ superstructure takes place on increasing the annealing temperature from 450 to 750°C. In contrast, a loss of ordering is found for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ when the preparation temperature increases from 700 to 800°C. From EPR spectra it is shown that the apparent g -factor is more sensitive towards the magnetic dilution of the Ni^{2+} sublattice by Mg^{2+} or $\text{Mg}^{2+}/\text{Ni}^{2+}$, while the line width undergoes little change. Electrochemical lithium extraction in the 5-V region was hindered by the presence of large amounts non-electroactive Mg^{2+} ions. Lithium extraction from $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ leads to a loss of intensity in the EPR signal as a consequence of the oxidation of paramagnetic Ni^{2+} to diamagnetic Ni^{4+} without significant changes in local environment of Mn^{4+} . For fully delithiated $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ oxide, the EPR spectrum from localised Mn^{4+} ions is observed, indicating an exhaustion of paramagnetic Ni^{2+} ions in the vicinity of Mn^{4+} ions. Microstructural and electro-chemical properties of $\text{LiCo}_x\text{Fe}_y\text{Mn}_{2-(x+y)}\text{O}_4$ compounds are also discussed.

Manganese-containing spinels are used as high voltage-electrodes in lithium-ion batteries [1–5]. Structural information based on X-ray and neutron diffraction has revealed cation ordering in the spinel structure. This effect leads to the appearance of a superstructure, which can be indexed in the $\text{P4}_3\text{32}$ space group and is dependent on the magnesium content and the preparation temperature. Thus, on decreasing the Ni/Mg ratio and on increasing the annealing temperature from 450 to 750°C for $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$, low-intensity superstructure lines become visible. The XRD pattern of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiMg}_{0.25}\text{Ni}_{0.25}\text{Mn}_{1.5}\text{O}_4$ samples could be indexed in Fd3m corresponding to a high purity spinel phase. In the cubic spinel notation, the lattice constant increases with the Mg amount in $\text{LiMg}_y\text{Ni}_{0.5-y}\text{Mn}_{1.5}\text{O}_4$

compositions: $a = 8.153 \text{ \AA}$; $a = 8.180 \text{ \AA}$, and $a = 8.193 \text{ \AA}$ for $y = 0, 0.25$, and 1.0 , respectively. For $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$, new reflections occur, which are ascribable to a $\text{P4}_3\text{32}$ lattice derived from Mg and Mn ordering in 16d sites of the initial Fd3m structure. The extent of metal ordering in the end members was also examined as a function of preparation temperature. For $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$, significant changes are visible in the X-ray diffraction patterns obtained for samples annealed between 400 and 800°C. On increasing preparation temperature up to 750°C, an increase in the intensity of the

superstructure lines is observed, while the changes are less obvious from 750 to 800°C. To overcome the difficulties related to the similar X-ray scattering factors of Mn and Ni, neutron diffraction was used to study $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. In this sample, a decrease in the intensity and increase in line broadening is observed on increasing preparation temperature. Thus, temperature and annealing time, as well as the presence of other elements such as Ti [1] and Co [2], condition the development of ordering in these systems. Neutron diffraction patterns (D1A instrument) for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ obtained at 700 and 800°C showed loss of ordering when the temper-

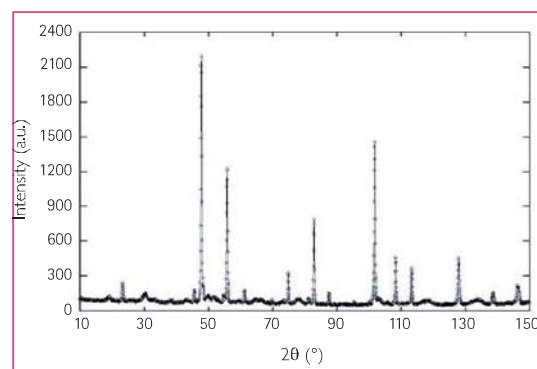


Figure 1: Neutron diffraction patterns of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ obtained at 800°C.

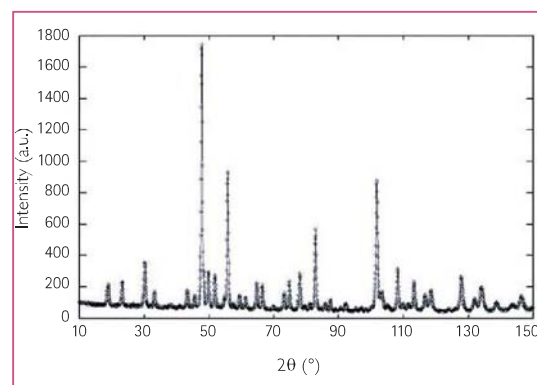


Figure 2: Neutron diffraction pattern of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ obtained at 700°C showing additional lines due to a $\text{P4}_3\text{32}$ superstructure.

ature of synthesis was higher (figures 1 and 2). From the well-resolved FTIR spectra, the Ni and Mg cation distribution could be concluded [3].

Electrochemical lithium de-intercalation from $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ takes place through a two-phase mechanism at ca. 4.7 V, involving the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple and showing a reversible specific capacity of about 130 mAh/g. The extension of the 4.7 V region decreases with increasing Mg-content. Nevertheless, cycling in the 3 V region, which implies lithium insertion in octahedral sites (16d) along with Mn^{4+} reduction to Mn^{3+} , leads to an extended plateau in which capacity increased with annealing temperature for $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples (figure 3).

The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ compound shows a ferromagnetic order in the spinel structure below $T_N = 130$ K. Above the magnetic ordering temperature, some residual anti-ferromagnetic $\text{Ni}^{2+}-\text{O}^{2-}-\text{Mn}^{4+}$ interactions are preserved, culminating at $T > 450$ K in the paramagnetic state. The EPR spectrum of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, recorded in the 140–410 K range consists of resonance absorption characterised by a Lorentzian line shape. On cooling, there is a strong resonance shift, with the apparent g-factor changing from 2.022 to 1.946. In the same temperature range, line narrowing takes place [3]. The signal disappears below 150 K. Thus, the EPR response from $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ can be associated with the residual anti-ferromagnetic correlations between Ni^{2+} and Mn^{4+} ions. The EPR spectra of Ni-Mg-Mn spinel oxides show significant changes

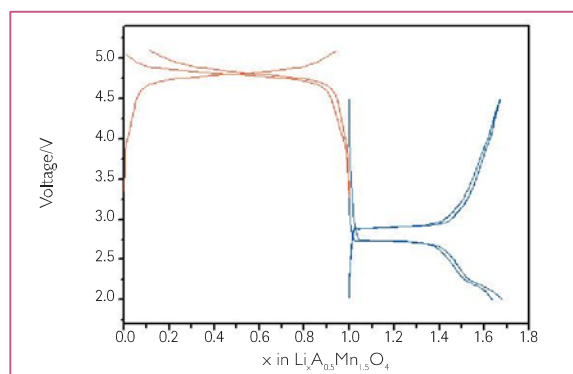


Figure 3: Typical voltage-curves for $\text{Li}_x\text{Mg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (blue line) and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (red line).

in resonance shift when diamagnetic Mg^{2+} ions substitute paramagnetic Ni^{2+} ions in the spinel framework [3]. The changes in line-width are less abrupt. The EPR behavior of $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is determined from localized Mn^{4+} ions. The extraction of lithium from $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples leads to EPR signal intensity loss as a consequence of the oxidation of paramagnetic Ni^{2+} by diamagnetic Ni^{4+} without significant changes in local environment. The fully delithiated oxide shows a different spectrum exclusively caused by Mn^{4+} ions but different to that of $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples also ascribed to this ion. The predominance of superexchange ferromagnetic interactions in the latter would justify the different profiles. Li reinsertion in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ shows a good recovery of the initial properties, making evident the notorious reversibility of this cathode material.

Rietveld refinement of neutron diffraction patterns of $\text{LiCo}_{0.2}\text{Fe}_{0.2}\text{Mn}_{1.6}\text{O}_4$ (Fd3m s. g.) shows that best fitting is obtained when 8a site occupancy is restricted to lithium

ions [2]. The refinement shows the complete occupancy of 16d sites by cobalt, iron, and manganese ions in stoichiometric ratios. For $\text{LiCo}_x\text{Fe}_y\text{Mn}_{2-(x+y)}\text{O}_4$ compounds the incorporation of iron and cobalt in the manganese spinel changes the shape of the voltage vs capacity curves in both the charge and discharge branches. Thus, for a manganese substitution lower than one manganese per formula ($x + y < 1$) an extended pseudo-plateau at ca. 4 V is observed, which corresponds to oxidation from Mn^{3+} to Mn^{4+} [2]. A maximum reversible capacity of ca. 130 mAh/g is achieved for $\text{LiCo}_{0.2}\text{Fe}_{0.2}\text{Mn}_{1.6}\text{O}_4$ in the complete potential range, including 4- and 5-V pseudo-plateaux. However, the progressive substitution of manganese (up to $x + y = 1$) results in a reduction of the 4-V region and an increase of the extension of a 5-V pseudo-plateau. For $\text{LiCo}_{0.8}\text{Fe}_{0.2}\text{MnO}_4$, ^{57}Fe Mössbauer spectra reveal high-spin Fe^{3+} ions in octahedral coordination in the pristine sample, which are oxidized to tetravalent iron ions upon electrochemical lithium extraction near 5 V and through a single cubic phase mechanism [2, 5].



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