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Improved layered mixed transition metal oxides for Li-ion batteries

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ABSTRACT

Recent work in our laboratory has been directed towards development of mixed layered transition metal oxides with general composition $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ ($\text{M}=\text{Al}, \text{Ti}$) for Li ion battery cathodes. Compounds such as $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ (often called NMCs) are currently being commercialized for use in consumer electronic batteries, but the high cobalt content makes them too expensive for vehicular applications such as electric vehicles (EV), plug-in hybrid electric vehicles (PHEVs), or hybrid electric vehicles (HEVs). To reduce materials costs, we have explored partial or full substitution of Co with Al, Ti, and Fe. Fe substitution generally decreases capacity and results in poorer rate and cycling behavior. Interestingly, low levels of substitution with Al or Ti improve aspects of performance with minimal impact on energy densities, for some formulations. High levels of Al substitution compromise specific capacity, however, so further improvements require that the Ni and Mn content be increased and Co correspondingly decreased. Low levels of Al or Ti substitution can then be used offset negative effects induced by the higher Ni content. The structural and electrochemical characterization of substituted NMCs is presented in this paper.

Keywords: Cathodes, metal oxides, Li ion batteries, Al-substitution, Ti-substitution

1. INTRODUCTION

Layered mixed transition metal oxides with the general formula $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ (NMCs) are currently being developed for use as cathodes in Li ion batteries. An idealized structure is shown in Figure 1. For most formulations, $x=z$ in these compounds, and only Ni and Co are electroactive, whereas Mn has the nominal oxidation state of +4 and is electrochemically inert. In principle the composition (i.e., x , y , and z) can be varied, but a number of trade-offs exist. An increase in the Ni and Mn contents lowers raw materials costs, but can result in poorer rate capability and thermal tolerance at high states of charge. Co improves rate capability but is expensive compared to Ni and Mn. Cost is a particularly important consideration for vehicular applications (plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs)), so reduction of Co content is a paramount concern. $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ is perhaps the most well-known of the NMCs and shows excellent performance. For example, it can deliver 150 mAh/g between 2.5 and 4.2 V vs lithium and close to 200 mAh/g when the charge is increased to 4.6 V.^{1, 2, 3, 4, 5} The power capability exceeds the high-power pulse requirement for hybrid vehicle applications,⁶ and the material shows increased thermal abuse tolerance compared to $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$.⁷ The relatively high Co content in this material and its associated cost has led researchers towards exploring different formulations such as $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ ⁸ and $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$.⁹ In the NMCs, Co is used to suppress migration of Ni into the Li sites,¹⁰ which adversely affects rate capability. In general, as the cobalt content is decreased, the degree of anti-site mixing increases. For example, in the parent, $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$, the amount of exchange can be as high as 12%,¹¹ leading to low rate capability for this material. Moreover, materials with increased Ni content may exhibit lower thermal stability at high states of charge.^{12, 13} These observations led us towards the exploration of partial or full substitution of Co with Al, Ti, or Fe in NMCs.^{14, 15} In some cases, substitution with these metals actually led to improvements in electrochemical behavior, suggesting that it may be possible to reduce Co in these compositions without compromising performance. An overview and summary of the work on substituted NMCs from our laboratory is presented in this paper.

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Figure 1. The idealized structure of layered NMCs. Li ions are represented as spheres. MO₆ octahedra connect to form the transition metal layers between the Li ion layers.

2. EXPERIMENTAL

Positive electrode materials were synthesized by the glycine-nitrate combustion procedure,¹⁶ as described previously.^{14, 15} Powder X-ray diffraction (XRD) patterns were used to confirm the structures of the calcined powders and were obtained on a Phillips X'Pert diffractometer equipped with an X'Celerator detector using Cu K α radiation. Rietveld refinements were carried out using the General Structure Analysis System (GSAS/EXPGUI) software package or the WINPLOTR/FullProf suite. Chemical analyses were carried out by Desert Analytics Laboratory (Tucson, AZ) to confirm nominal compositions. Pressed pellets for conductivity studies were made as described previously.¹⁵ AC impedance spectra were obtained using a Solartron Instruments 1260 impedance/gain-phase analyzer. Conductivities were derived from the intercept of the capacitive arc with the Z' axis in the Nyquist plots.

Laminate composite electrodes comprised of 84 wt % active material, 8 wt % polyvinylidene fluoride (PvDF, Kureha Chemical Ind. Co. Limited), 4 wt % Denka compressed acetylene black, and 4 wt % SFG-6 synthetic flake graphite (Timcal Ltd., Graphites and Technologies) were prepared by applying slurries in 1-methyl-2-pyrrolidinone onto carbon-coated current collectors (Intelicoat Technologies) by automated doctor blade. After drying in air and in vacuum for at least 24 h, 1.8 cm² electrodes having an average loading of 7–10 mg/cm² of active material were punched out. Coin cells (2032 size) containing these electrodes were assembled in a helium-filled glove box with lithium metal anodes and 1 M LiPF₆ in 1:2 ethylene carbonate/dimethyl carbonate electrolyte solution (Ferro). Galvanostatic cycling was carried out on an Arbin BT/HSP-2043 cycler between limits of 2.0 and 4.3–4.7 V or a VMP3 potentiostat/galvanostat (Bio-Logic). *In situ* X-ray diffraction patterns were obtained on Li cells containing composite electrodes at the Stanford Synchrotron Radiation Lightsource on beamline 11-3.

3. RESULTS AND DISCUSSION

The theoretical capacities of most NMCs are about 270 mAh/g. EXAFS studies have shown that electrochemical processes below about 4.3V vs. Li are dominated by the redox chemistry of $\text{Ni}^{2+} \leftrightarrow \text{Ni}^{4+}$, while Co is oxidized primarily at higher voltages.^{17, 18, 19} The charge potential is generally limited to about 4.3V vs. Li in practical cells to prolong cycle life. Thus, even if the substituent is electrochemically inactive, replacement of Co should have little impact on practical energy density, provided no other changes occur. Figure 2 shows the effect of substitution of Al, Ti, and Fe on the theoretical capacities of several series of NMCs, as well as capacities obtained in lithium cells discharged at 0.1 mA/cm² between 4.3 and 2.0V.

For the unsubstituted NMCs, raising the Ni and Mn contents and lowering the Co contents in cathode materials decreases the discharge capacity obtained in lithium cells somewhat (compare Figures 2a, 2b, and 2c). In the case of $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$, the obtained discharge capacity nearly matches what is predicted based on the Ni content, but the discrepancy widens for $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ and even more so for $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$. This most likely reflects increases in ion-mixing (i.e., Ni in 3a sites) as the Co content is decreased. For all three series, Al substitution lowers the practical discharge capacity obtained during discharge in lithium cells, but the effect is most severe for the $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3-y}\text{Al}_y\text{Mn}_{1/3}]\text{O}_2$ materials. A 15% decrease is observed for $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/6}\text{Al}_{1/2}\text{Mn}_{1/3}]\text{O}_2$ over the parent compound, compared to 7% for $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.1}\text{Al}_{0.1}\text{Mn}_{0.4}]\text{O}_2$ and $\text{Li}[\text{Ni}_{0.45}\text{Al}_{0.1}\text{Mn}_{0.45}]\text{O}_2$ over the unsubstituted analogs. The larger than expected drop in discharge capacity is primarily caused by a rise in the average voltage potential upon charge induced by the Al substitution, which decreases the amount of Li that can be extracted below 4.3V. A similar increase in the discharge potential is also observed, indicating that the cause is thermodynamic, rather than kinetic.

Low levels of Fe substitution also results in a severe drop in discharge capacity, especially for $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/6}\text{Fe}_{1/12}\text{Mn}_{1/3}]\text{O}_2$ (see Figures 2d and 2f), while the effect of Ti substitution has very little impact on utilization. Interestingly, Fe substitution does not have a big effect on the overall theoretical capacity, assuming that the $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox couple is active. Although Ti most likely substitutes in as electrochemically inert Ti^{4+} , some Mn^{4+} must be converted to electroactive Mn^{3+} for charge compensation (there is no evidence of Li deficiency in the $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/6}\text{Ti}_{1/12}\text{Mn}_{1/3}]\text{O}_2$ material); thus the overall theoretical capacity is also nearly unaffected.

The nature of the substituent and the overall composition of the materials affect other aspects of the electrochemical performance in lithium cells. Iron substitution not only results in decreases in capacity but also has deleterious effects on rate capability and appears to increase capacity fading upon cycling.^{14, 15} In contrast, Ti and Al substitution appear, at least for some cases, to improve both rate capability and cycling stability. A comparison of the cycling behaviors of $\text{Li}/\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ and $\text{Li}/\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.15}\text{Al}_{0.05}\text{Mn}_{0.4}]\text{O}_2$ cells are shown in Figure 3. Although substitution with Al decreases the capacity somewhat, this disadvantage is erased by about the 25th cycle due to the improved cycling. The wide variation in behavior observed upon substitution with different metals is somewhat surprising and bears further investigation.

Both Al and Fe substitution in the $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2-y}\text{M}_y\text{Mn}_{0.4}]\text{O}_2$ series cause a decrease in the conductivity (Figure 4). Al is an sp-type metal, with no d-electrons available near the Fermi state, so a decrease in electronic conductivity is expected. The result for Fe is particularly dramatic and more difficult to explain, but may be caused by disruption of the cobalt bonding network induced by the substitution. Materials with poor conductivity can sometimes perform extremely well in electrochemical cells, (e.g., LiFePO_4 with $\sigma_{\text{RT}}=10^{-9}$ S/cm²⁰). In fact, $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.1}\text{Al}_{0.1}\text{Mn}_{0.4}]\text{O}_2$, which has an equally low conductivity as $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.15}\text{Fe}_{0.05}\text{Mn}_{0.4}]\text{O}_2$, has much better discharge characteristics. Thus, alternative explanations must be sought for the latter's poor electrochemical behavior.

Structural changes induced by partial or full substitution of Co in the NMCs may be responsible for some of the differences in electrochemical behavior.^{14, 15} It has already been noted that high concentrations of anti-site defects in NMCs impede lithium diffusion and result in poor rate capability. Such defects decrease the layered character of the structures. The c/3a ratio (where a and c are unit cell parameters) has often been taken as a qualitative measure of lamellarity.^{10, 21} These values can range from 1.793 for an ideal layered structure (i.e., LiTiS_2) to 1.633 for cubic close-packed structures (e.g., complete disorder). Layered materials containing defects will fall somewhere in between these values. The c/3a ratios for baseline materials and substituted NMCs are summarized in Figure 5.

Figure 2. Effect of substitution for cobalt on the theoretical capacities of $\text{Li}[\text{Ni},\text{Co},\text{M},\text{Mn}]\text{O}_2$ ($\text{M}=\text{Al}, \text{Fe}, \text{or Ti}$) materials: (a) $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3-y}\text{Al}_y\text{Mn}_{1/3}]\text{O}_2$, (b) $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2-y}\text{Al}_y\text{Mn}_{0.4}]\text{O}_2$, (c) $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1-y}\text{Al}_y\text{Mn}_{0.45}]\text{O}_2$, (d) $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3-y}\text{Fe}_y\text{Mn}_{1/3}]\text{O}_2$, (e) $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3-y}\text{Ti}_y\text{Mn}_{1/3}]\text{O}_2$, and (f) $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2-y}\text{Fe}_y\text{Mn}_{0.4}]\text{O}_2$. The capacities obtained in Li cells discharged at 0.1 mA/cm^2 between 4.3 and 2.0V are also shown.

Figure 3. Discharge capacity as a function of cycle number for $\text{Li}/\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ and $\text{Li}/\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.15}\text{Al}_{0.05}\text{Mn}_{0.4}]\text{O}_2$ cells cycled at 0.1 mA/cm^2 between 4.3 and 2.0V.

Figure 4. Conductivities of $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2-y}\text{M}_y\text{Mn}_{0.4}]\text{O}_2$ (M=Al, Fe) pressed pellets at 75°C .

Figure 5. $c/3a$ ratios, obtained from Rietveld refinements of XRD power patterns of substituted NMCs. In the legend, 424-Al and 424-Fe refer to the $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2-y}\text{M}_y\text{Mn}_{0.4}]\text{O}_2$ ($\text{M}=\text{Al}$ or Fe) series while 333-Al, 333-Fe, and 333-Ti refer to the $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3-y}\text{M}_y\text{Mn}_{1/3}]\text{O}_2$ ($\text{M}=\text{Al}$, Fe , or Ti) respectively.

The lower $c/3a$ ratio of the baseline $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ compound compared to the baseline $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ (left side of Figure 5) is consistent with the electrochemical results and previous observations of increased ion mixing as Co content is decreased. Refinements of combined powder neutron and XRD patterns on $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$ show that approximately 6.6% of the Ni is located on Li sites.¹⁵ Figure 5 also shows that Al or Ti substitution improves the layered character, whereas Fe substitution has the opposite effect. In $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.15}\text{Fe}_{0.05}\text{Mn}_{0.4}]\text{O}_2$, the concentration of anti-site defects increases to 7.2%. Thus, the poor electrochemical behavior of this compound may be attributable to the increased ion mixing and effect this has on lithium diffusion. However, Al substitution in this series also appears to increase the amount of Ni on Li sites marginally, seemingly contrary to the qualitative results shown in Figure 5. The better lamellarity of these materials appears to be caused mainly by an opening up of the Li slab spacing (LiO_2), which is associated with faster lithium diffusion²² (Figure 6). This phenomenon is associated with changes in the overall bond covalencies upon substitution. The average M-O bond lengths decrease with higher Al content, causing the transition metal slab thickness to decrease and the Li-O bonds to lengthen. Interestingly, these effects are more apparent in the $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3-y}\text{Al}_y\text{Mn}_{1/3}]\text{O}_2$ series than in the $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2-y}\text{Al}_y\text{Mn}_{0.4}]\text{O}_2$ system. While it is likely that the increase in the lithium slab spacing can compensate for the negative effects on lithium diffusion rates of a minor increase in anti-site mixing, the smaller change seen in the $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2-y}\text{Al}_y\text{Mn}_{0.4}]\text{O}_2$ series runs contrary to the observation that Al substitution actually has more beneficial effects than in the $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3-y}\text{Al}_y\text{Mn}_{1/3}]\text{O}_2$ materials, especially on rate capability. However, Figures 5 and 6 show values only for the fully lithiated materials and no information on how $c/3a$ and LiO_2 slab spacings vary as a function of state-of-charge.

GITT experiments carried out on cells containing $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.2-y}\text{Al}_y\text{Mn}_{0.4}]\text{O}_2$ electrodes show that Li diffusion coefficients vary by as much as an order of magnitude as a function of lithium content.¹⁵ For all materials, regardless of degree of Al substitution, values reach maxima at compositions of about $x=0.5-0.6$ and then fall off precipitously as lithium is further extracted. This roughly corresponds to the behavior of the c lattice parameter upon delithiation of NMCs. For example, Figure 7 shows the variation in the d_{003} spacing of $\text{Li}_x[\text{Ni}_{0.45}\text{Co}_{0.05}\text{Al}_{0.05}\text{Mn}_{0.45}]\text{O}_2$ as x is varied in by discharging a lithium battery *in situ* at the Stanford Synchrotron Radiation Lightsource. The d_{003} spacing is 1/3 of the value of the c lattice parameter, which is influenced by both the size of the LiO_2 slab and the MO_2 transition metal slab thickness. Further analysis of these data should allow these values to be extracted as a function of Li content and composition of the NMCs, allowing a more complete picture to be obtained of how substitution influences structure and electrochemical behavior of these cathode materials.

Figure 6. Variation of the LiO₂ slab spacing for Li[Ni_{0.4}Co_{0.2-*y*}Al_{*y*}Mn_{0.4}]O₂ and Li[Ni_{1/3}Co_{1/3-*y*}Al_{*y*}Mn_{1/3}]O₂ materials.

Figure 7. The change in the d₀₀₃ spacing of Li_{*x*}[Ni_{0.45}Co_{0.05}Al_{0.05}Mn_{0.45}]O₂ as *x* is varied by charging a lithium cell containing this material *in situ*.

4. CONCLUSIONS

The purpose of this work has been to investigate the feasibility of replacing all or part of the expensive cobalt in the layered mixed transition metal compounds known informally as NMCs, with lower cost metals. The effect of these substitutions upon the electrochemical behavior varies widely depending upon the composition, amount, and nature of the substituent in ways that are not always expected. For example, iron substitution has particularly deleterious effects on electrochemical performance, even though it is expected to be electroactive and does not decrease the theoretical capacity. The substitution of Fe for Co in the NMCs decreases the layered character by increasing the amount of Ni on the Li sites, which adversely affects Li diffusion. In contrast, both Al and Ti substitution, which are not electroactive have some beneficial effects, although practical capacities are decreased in the case of the former. Both of these metals improve lamellarity, although Al does so mainly by increasing the LiO_2 slab spacing, rather than decreasing disorder. The degree of the effect of Al on the structures of the as-made materials differs depending upon the overall composition, however, and does not necessarily track the relative improvements in electrochemical performances. A possible explanation is that LiO_2 slab spacings change in different ways as a function of state-of-charge for different series. Further work will be directed towards understanding and exploring these possibilities.

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