Layered Manganese Oxide Intergrowth Electrodes for Lithium Batteries

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Several layered and tunnel-structured lithium manganese oxides not available by direct synthesis may be prepared by ion-exchange of sodium-containing precursors.[1] Included among these are compounds with the stacking sequences shown in Figures 1a and b. Those having O'3 or O3 stacking sequences (Figure 1a) readily convert to spinel upon cycling in lithium cells,[2] but O2 compounds (Figure 1b) prepared from P2 sodium-containing precursors do not.[3,4]

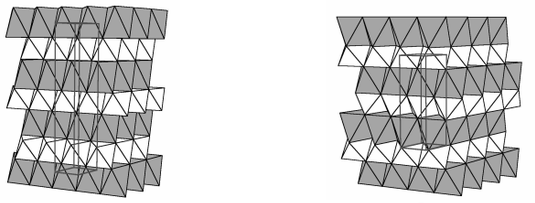

Figure 1. a) O3 structure (space group $R\bar{3}m$) and b) O2 structure (space group $P6_3mc$). Alkali metal ion layers are shaded gray, transition metal layers are white, and dark gray lines show unit cell outlines.

We have recently discovered a class of layered manganese oxides that are intergrowths of structures 1a and b,[5] having the general formula $Li_xM_yMn_{1-y}O_{2+z}$ (M=Ni, Co, Al, Li or Fe, $x \approx 0.5$-0.8, $y \leq 0.4$, and $z \approx 0$-0.05). The composition range for the intergrowths is determined by the amount and nature of the substituent as well as the Na/transition metal ratio (Figure 2).

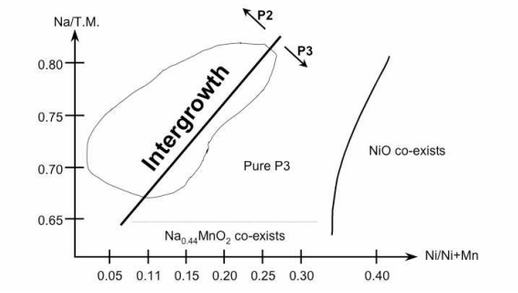

Figure 2. Phase diagram showing approximate composition range of P2/P3 intergrowths in the Na-Ni-Mn-O system. Upon ion exchange P2 components convert to O2 and P3 to O3.

Electrodes with greater amounts of O3 component show better electrochemical properties (higher capacity and rate capability) than those with less.[6] Interestingly, recent ^{7}Li-MAS NMR experiments on cycled intergrowth electrodes show loss of the signal due to Li in an O3 environment but no concomitant growth of a signal due to Li in a spinel environment.[5] The O2 component appears to impede the long range ordering necessary to form crystalline spinel, although some cation rearrangement in the O3 component does take place. Differential capacity plots of data from a lithium cell containing O2/O3-$Li_xAl_{0.15}Mn_{0.85}O_2$ undergoing galvanic charge and discharge show evidence of partial spinel conversion after 100 cycles, but the discharge profiles still primarily resemble those of layered compounds (Figure 3).

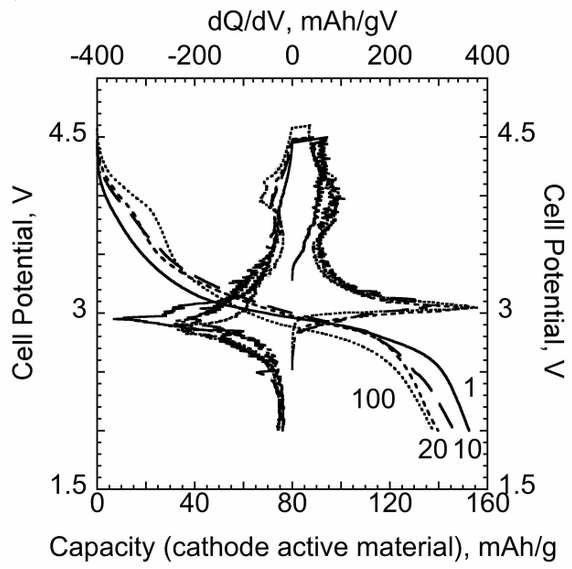

Figure 3. Discharges of an O2/O3-$Li_xAl_{0.15}Mn_{0.85}O_2$/Li cell at 0.055 mA/cm^2. Differential capacity data from the full cycles are also shown.

These results suggest it may be possible to design high capacity layered manganese oxide electrodes that are reasonably stable against spinel conversion.

Acknowledgments

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References

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