Layered $Li(Mn_{0.5-x}Ni_{0.5-y}M'_{x+y})O_2$ (M'=Al, Ti) Cathode Materials for Rechargeable Lithium Batteries

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Layered $Li(Mn_{0.5}Ni_{0.5})O_2$ is attractive cathode material for rechargeable lithium batteries in terms of cost and safety. Furthermore, it does not convert to a spinel compound during electrochemical cycling [1,2] and the material is expected to be more environmentally benign and more thermally stable than $LiNiO_2$ because of its higher Mn and lower Ni content.

In this work, $Li(Mn_{0.5-x}Ni_{0.5-y}M'_{x+y})O_2$ (M'=Al, Ti) materials with α-$NaFeO_2$ structure were synthesized using a mixed hydroxide precursor, $(Mn_{0.5}Ni_{0.5})(OH)_2$.

Appropriate amounts of LiOH, $(Mn_{0.5}Ni_{0.5})(OH)_2$, $Al(OH)_3$, and TiO_2 were mixed and calcined at 1000 ^oC for 15-24 h. The powder X-ray diffraction patterns of $Li(Mn_{0.475}Ni_{0.475}M'_{0.05})O_2$ (M'=Al, Ti) are shown in Fig. 1. All of the peaks could be indexed based on the $R\bar{3}m$ structure, which indicates that the synthesized materials were phase-pure, layered structure.

In Fig. 2 are shown discharge capacities of Li/ $Li(Mn_{0.475}Ni_{0.475}M'_{0.05})O_2$ (M'=Al, Ti) cells as a function of cycle number. Both of the materials exhibit good cycleability at 2.8-4.3 and 2.8-4.6 V.

Cyclic voltammetry curves from $Li(Mn_{0.475}Ni_{0.475}M'_{0.05})O_2$ (M'=Al, Ti) are shown in Fig. 3. Both of the materials show a major peak centered at 3.9-4.0 V and a small, broad peak at *ca.* 4.4 V upon charging. The absence of multiphase reactions suggests that severe structural degradation is not expected during electrochemical cycling of $Li(Mn_{0.475}Ni_{0.475}M'_{0.05})O_2$ (M'=Al,Ti). Furthermore, no redox peaks are observed in the 3 V range where Mn^{+3}/Mn^{+4} redox reaction is reported to occur in the layer-structured $Li_{2/3}(Ni_{1/3}Mn_{2/3})O_2$ [3], which suggests that Mn ions are electrochemically inactive and present as Mn^{4+} in $Li(Mn_{0.475}Ni_{0.475}M'_{0.05})O_2$ (M'=Al, Ti). Preliminary experiments of X-ray photoelectron spectroscopy and magnetic susceptibility measurements revealed that Mn ions are present as Mn^{4+} and Ni ions as Ni^{2+} in the layered structure.

Differential scanning calorimetry (DSC) profiles of $Li(Mn_{0.475}Ni_{0.475}Al_{0.05})O_2$ samples are shown in Fig.4 with those of $Li(Ni_{0.8}Co_{0.2})O_2$ for comparison [4]. $Li(Mn_{0.475}Ni_{0.475}Al_{0.05})O_2$ has only one sharp exothermic peak at 270 ^oC. Heat associated with the exothermic peak of $Li(Mn_{0.475}Ni_{0.475}Al_{0.05})O_2$ is 534J/g, less than half that of the heat generated by the $Li(Ni_{0.8}Co_{0.2})O_2$. These data indicate that the safety characteristics of $Li(Mn_{0.475}Ni_{0.475}Al_{0.05})O_2$ are superior to those of $Li(Ni_{0.8}Co_{0.2})O_2$.

In conclusion, layered $Li(Mn_{0.475}Ni_{0.475}M'_{0.05})O_2$ (M'=Al, Ti) are promising candidates for cathode materials of rechargeable lithium batteries in terms of cost, cycling stability, and thermal safety.

Reference

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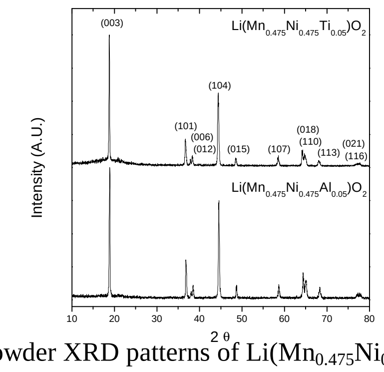

Fig. 1. Powder XRD patterns of $Li(Mn_{0.475}Ni_{0.475}Ti_{0.05})O_2$ and $Li(Mn_{0.475}Ni_{0.475}Al_{0.05})O_2$.

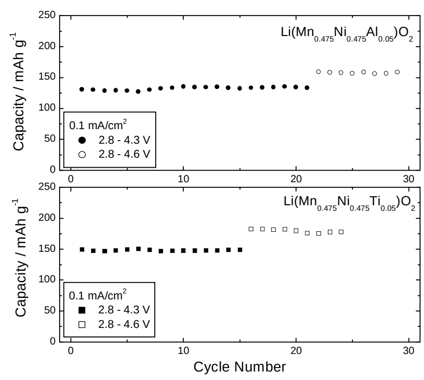

Fig. 2. Discharge capacities of Li/ $Li(Mn_{0.475}Ni_{0.475}M'_{0.05})O_2$ (M'=Al, Ti) cells as a function of cycle number.

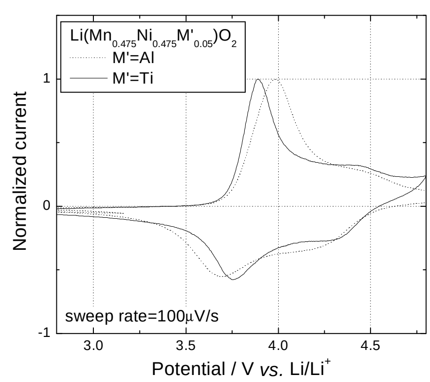

Fig. 3. Cyclic voltammetry profile of $Li(Mn_{0.475}Ni_{0.475}M'_{0.05})O_2$ (M'=Al,Ti) at a sweep rate of 100 μV/s.

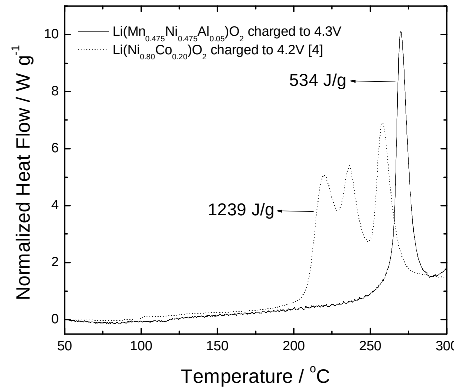

Fig. 4. Differential scanning calorimetry (DSC) profile (10 ^oC/min) of $Li(Mn_{0.475}Ni_{0.475}Al_{0.05})O_2$ charged to 4.3 V. DSC profile of $Li(Ni_{0.80}Co_{0.20})O_2$ charged to 4.2 V was taken from Ref.[4] for comparison.