

LiAl_yNi_{0.5-y}Mn_{1.5}O₄ (y = 0.0–0.4) AS 5-VOLT CATHODES FOR LITHIUM BATTERIES

G. Ting-kuo Fey*, Cheng-Zhang Lu and T. Prem Kumar#

Department of Chemical and Materials Engineering,
National Central University
Chung-Li, Taiwan 32054 R.O.C.

#On deputation from: Central Electrochemical Research
Institute, Karaikudi 630006, TN, India.

One method adopted to surmount the poor cyclability problem of LiMn₂O₄ is the partial substitution of the manganese with a metal ion that can stabilize the host structure during the charge-discharge processes. Although such substitutions can enhance the structural stability of the host structure, there is often a penalty in terms of the 4-volt capacity. This presentation reports the structural and lithium intercalation properties of LiAl_yNi_{0.5-y}Mn_{1.5}O₄ (y = 0.0, 0.1, 0.2, 0.3 and 0.4). The compositions were prepared by a solid-state fusion method from Li₂CO₃, MnO₂, NiO and Al(OH)₃ at 800°C for 24 h in air.

The x-ray diffraction peaks recorded for the Al-substituted compositions were indexable in the *Fd3m* space group. A few minor peaks also appeared, especially at the higher Al concentrations, suggesting the presence of some extraneous phases like γ -LiAlO₂ [1]. According to Ohzuku et al. [2] the integrated intensity ratios of the (400)/(311) and (220)/(311) peaks are indices of the occupancy of the substituent ions in the 8a lithium sites. An analysis of our XRD data showed increased occupancy of the substituent Al in the 8a lithium lattice sites especially at Al stoichiometries above 0.3.

The various compositions were cycled between 3.30 and 4.95 V at a 0.1 C rate in 2032-type coin cells with lithium as the anode. They showed two regions of electrochemical activity: one in the 4-volt region and the other in the 5-volt region. For comparison, the cycling performance (between 3.00 and 4.20 V) of an unsubstituted LiMn₂O₄ sample was also studied. Substituting the trivalent Al ion for Ni in LiNi_{0.5}Mn_{1.5}O₄ should result in the reduction of an equivalent amount of Mn⁴⁺ to Mn³⁺, yielding materials with increased 4-volt activity (Table 1). It can also be seen from Table 1 that the cumulative capacity of the spinel increases when the Ni content is increased from 0.1 to 0.5 atom/molecule. At the latter composition, theoretically, there is only one active species: the 5-volt-oxidizable Ni²⁺ species, whose two-electron transfer oxidation to Ni⁴⁺ should result in higher capacities. In fact, the first-cycle discharge capacity of LiNi_{0.5}Mn_{1.5}O₄ was 114 mAh/g as against 108 mAh/g for LiMn₂O₄. A first-cycle capacity of 110 mAh/g was obtained with LiAl_{0.1}Ni_{0.4}Mn_{1.5}O₄. Higher capacities at higher voltages should translate into higher power densities for the Ni-substituted spinels.

The results of extended cycling studies (Fig 1) show that the unsubstituted spinel gave a cumulative first-cycle discharge capacity of 108 mAh/g, which faded to 90 mAh/g in the 25th cycle, registering charge retention of 84%. The corresponding values for LiNi_{0.5}Mn_{1.5}O₄ were 114 and 110 mAh/g and 97%. Thus, substitution with Ni enhanced the first cycle capacity as well as the cyclability of the spinel. In the case of the Al-substituted compositions with y = 0.1, there was an initial surge in the capacity (110 mAh/g). However, as the y values were

increased, the capacities of the Al-substituted materials dropped. The fall in capacity with an increase in the y value is a consequence of the increased propensity of these ions to occupy the 8a lithium sites as their concentration is increased. Their occupancy in the lithium sites can impede transport of the Li ions during the charge-discharge processes. This is reflected in the decreased charge retention of the Al-substituted materials (e.g., 71% over 60 cycles for y = 0.1). Thus, Al does not seem to lead to structural stability. It was also observed that the capacities of the Al-substituted materials registered a general increase from the first cycle to the 10th, followed by a slow decay in subsequent cycles.

Acknowledgements

Financial support by the National Science Council of the Republic of China under contract NSC-90-2214-E-008-003 is gratefully acknowledged. TPK thanks the NSC for the award of a post-doctoral fellowship.

References

- [1] S.T. Myung, S. Komaba, N. Kumagai, J. Electrochem. Soc. **148** (2001) A482.
- [2] T. Ohzuku, K. Ariyoshi, S. Takeda, Y. Sakai, Electrochim. Acta **46** (2001) 2327.

Table 1. The theoretical and observed first-cycle capacities of the various LiAl_yNi_{0.5-y}Mn_{1.5}O₄ compositions

Composition	4-volt capacity		5-volt capacity		C. C.
	T. C.	O. C.	T. C.	O. C.	
LiMn ₂ O ₄	148.2	108.0	---	---	108.0
LiNi _{0.5} Mn _{1.5} O ₄	0.0	27.2	146.7	86.8	114.0
LiAl _{0.1} Ni _{0.4} Mn _{1.5} O ₄	14.9	37.1	119.4	72.9	110.0
LiAl _{0.2} Ni _{0.3} Mn _{1.5} O ₄	30.4	48.8	91.2	50.2	99.0
LiAl _{0.3} Ni _{0.2} Mn _{1.5} O ₄	46.4	58.9	61.9	38.1	97.0
LiAl _{0.4} Ni _{0.1} Mn _{1.5} O ₄	63.1	69.3	31.5	21.7	91.0

T. C. : Theoretical Capacity (mAh/g)

O. C. : Observed Capacity (mAh/g)

C. C. : Cumulative Capacity Observed (mAh/g)

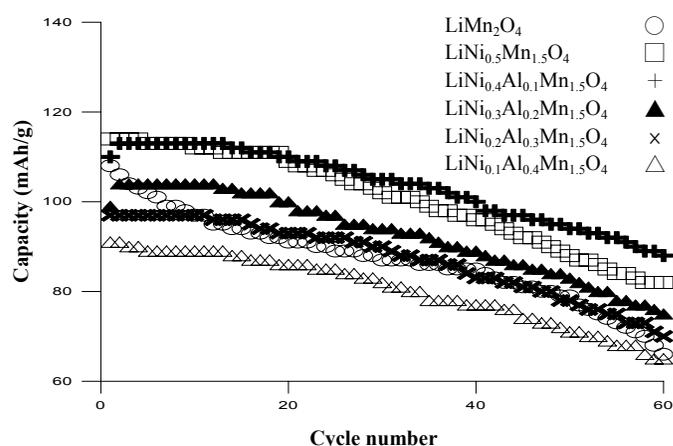


Fig. 1. Cycling behavior of the various doped systems