Lithium Manganese Oxide Spinel Cathode for Rechargeable Lithium Batteries

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Introduction

Spinel lithium manganese oxide has been studied extensively because of its high possibility of being commercialized as a cathode material for lithium-ion batteries. However, attempts to substitute $LiMn_2O_4$ for $LiCoO_2$ in commercial lithium-ion batteries have not been successful due to the lower specific capacity and the fast capacity fade upon cycling. To overcome these problems, partial substitution of manganese with other metals to make $LiM_xMn_{2-x}O_4$ (M = Co, Mg, Cr, Ni, Fe, Al, Ti, and Zn) has been suggested. In the case of a small amount of substitution, the dopant reduces the initial capacity at the 4 V plateau slightly, but improves the cycle life greatly [1]. By contrast, an extensive amount of substitution show significant decrease in capacity at the 4 V plateau due to the lack of Mn^{3+} content in the spinel [2]. Recently, researchers have shown that the significant capacity loss at the 4 V plateau reappears in a higher voltage, i.e., $LiCr_{0.5}Mn_{1.5}O_4$ at 4.8 V; $LiCu_{0.5}Mn_{1.5}O_4$ at 4.9 V; $LiCoMnO_4$ at 5.0 V; and $LiNi_{0.5}Mn_{1.5}O_4$ at 4.7 V [3-7]. Of them, only $LiNi_{0.5}Mn_{1.5}O_4$ shows acceptable stability with considerable capacity.

Spinel $LiNi_{0.5}Mn_{1.5}O_4$ has been studied by several groups [6,7]. Improved capacity and cycleability are reported in the material that was fired at higher temperature, though the reported capacity is still lower than its theoretical capacity of 149 mAh/g by about 40 mAh/g. On the other hand, the elevated firing temperature was reported to result in oxygen loss and Ni deficiency in $LiNi_{0.5}Mn_{1.5}O_4$ material, and hence reduces the length of 4.7 V plateau. Recently, H. Kawai et al. reported that the oxygen loss in conventional ceramic synthesis can be reduced greatly by a post-reaction annealing at $600^{\circ}C$ [5]. This prompted us to adopt high temperature firing condition and the post-reaction annealing procedure in the synthesis of $LiNi_xMn_{2-x}O_4$ (x = 0.5, 0.55, and 0.6) materials. In the current report, we have prepared and characterized $LiNi_xMn_{2-x}O_4$ (x =0.5, 0.55, and 0.6) that have superior capacity and stability to $LiMn_2O_4$.

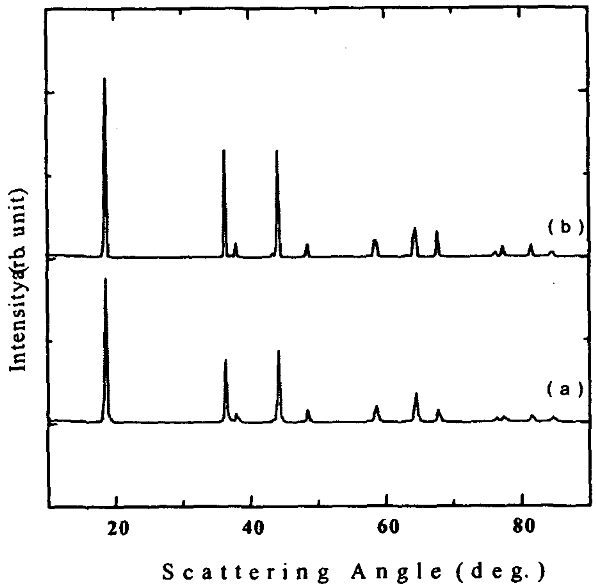
Experimental

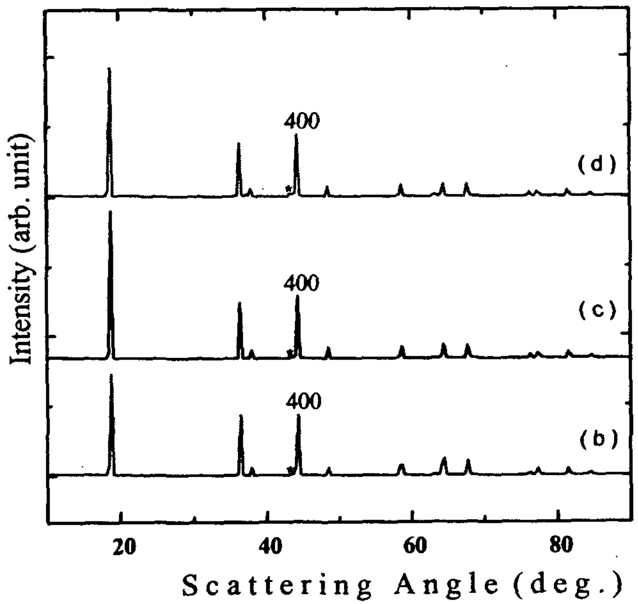
1. Synthesis: Gels obtained from $(CH_3CO_2)_2Mn \cdot 4H_2O$, $NiNO_3$, LiOH mixture
   Samples calcined at different temperatures

2. Characterization: Powder XRD, SEM, Raman, BET, SSCV, EIS

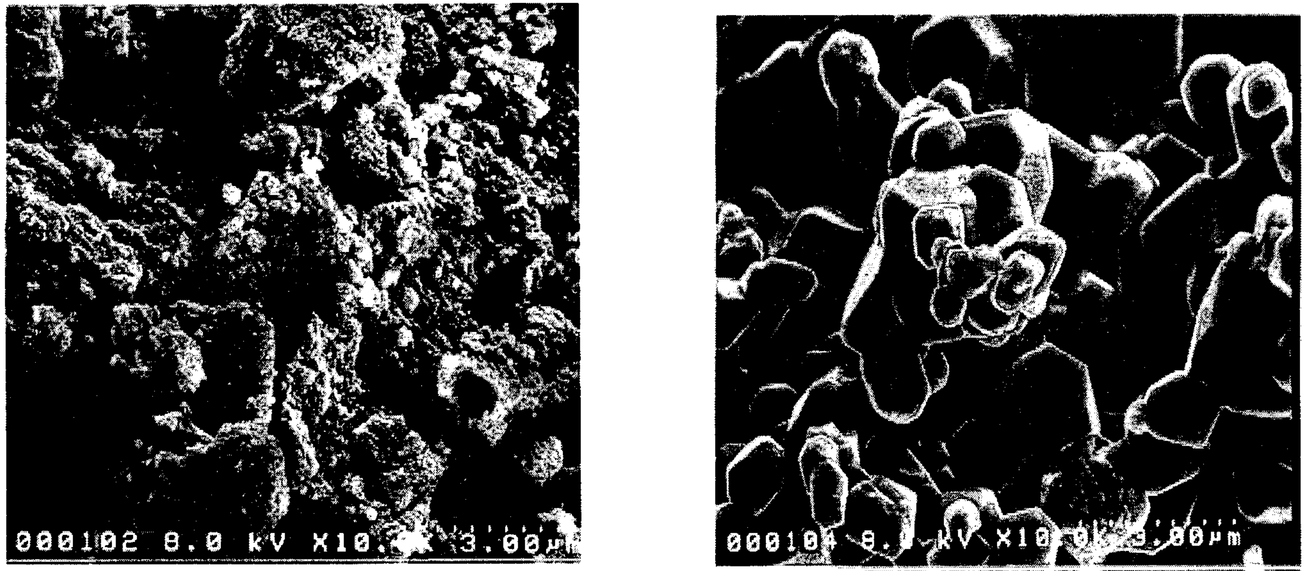
3. Electrode preparation: Spinel sample:TAB in 80:20 ratio, SSCC

4. Cell fabrication: As prepared electrode, Li metal, Separator, $LiPF_6$ - PC
   Hohsen 3 electrode cell: Li metal counter and reference



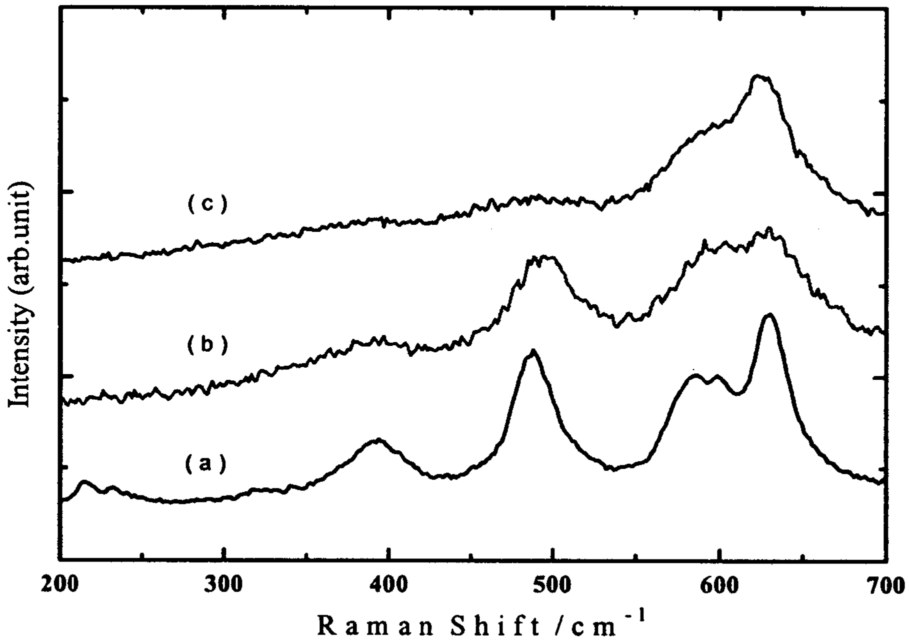


XRD patterns of (a) $LiNi_{0.5}Mn_{1.5}O_4$ calcined at 600°C, (b) $LiNi_{0.5}Mn_{1.5}O_4$ calcined at 850°C, (c) $LiNi_{0.55}Mn_{1.45}O_4$, and (d) $LiNi_{0.6}Mn_{1.4}O_4$.

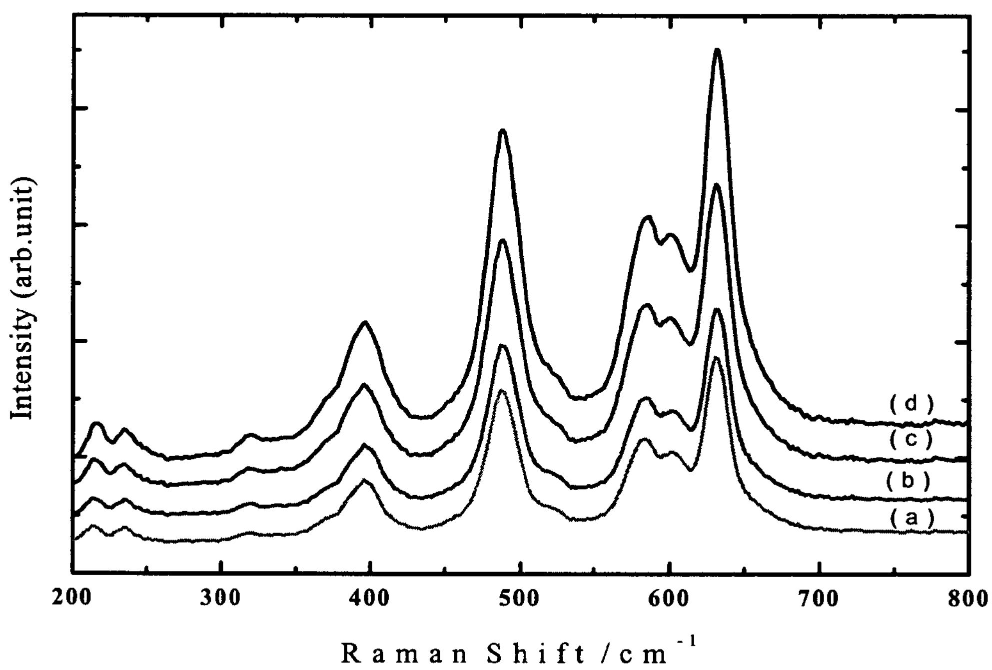


(a) (b)

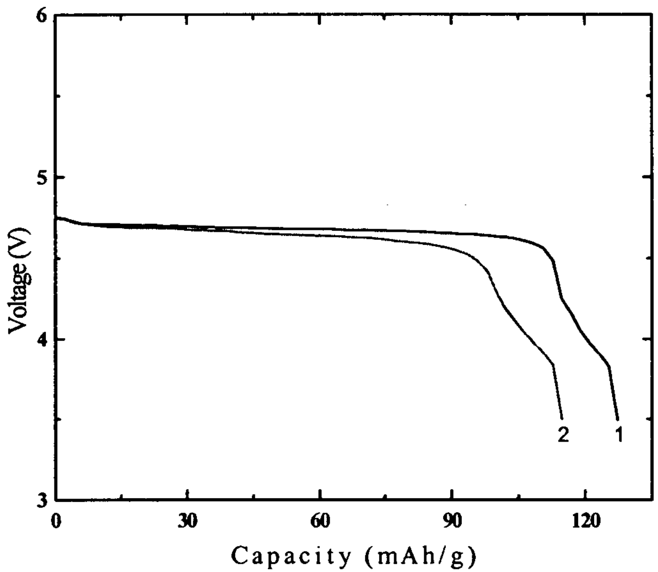
SEM images of spinel $LiNi_{0.5}Mn_{1.5}O_4$: (a) Calcined at 600°C and (b) Calcined at 850°C .



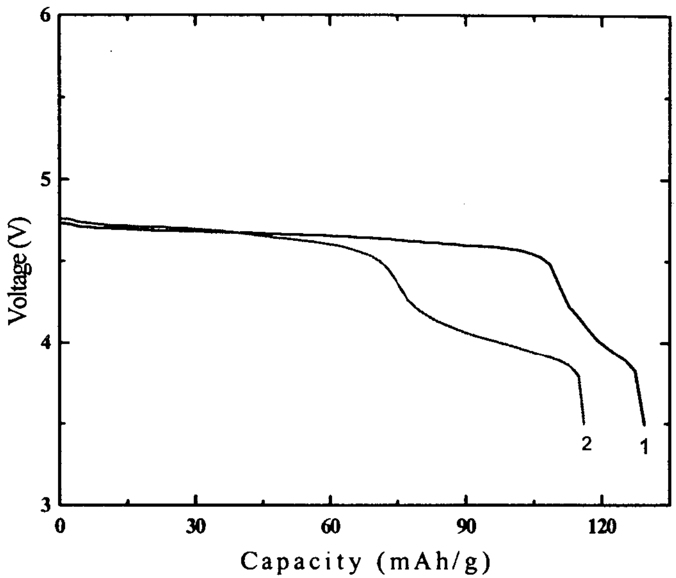
Raman spectra of (a) $LiNi_{0.5}Mn_{1.5}O_4$ calcined at $850^{o}C$, (b) $LiNi_{0.5}Mn_{1.5}O_4$ calcined at $600^{o}C$, and (c) $LiMn_2O_4$



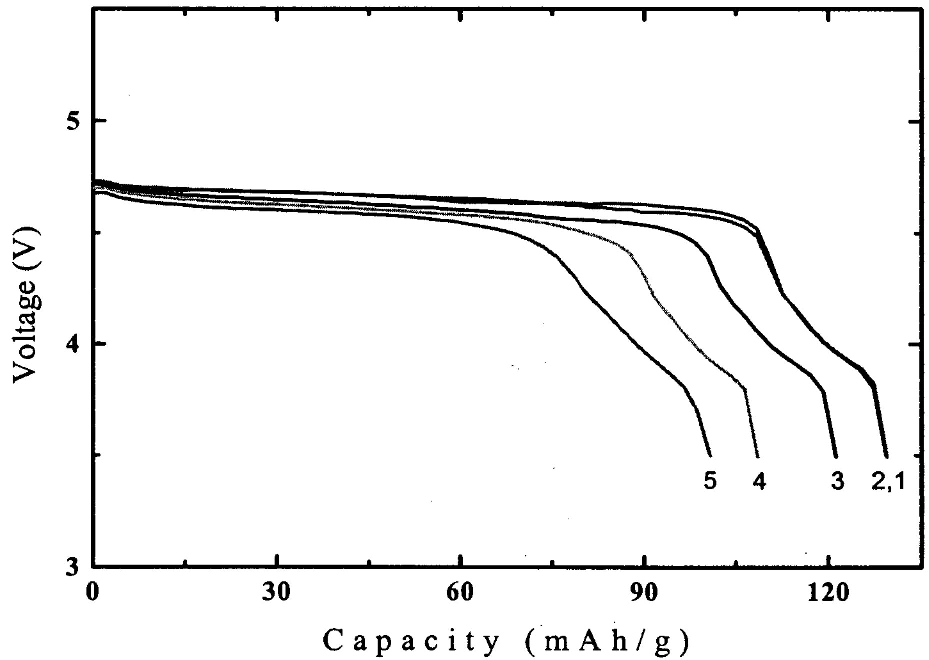
Raman spectra of $LiNi_{0.5}Mn_{1.5}O_4$ fired at (a) 750°C, (b) 800°C, (c) 850°C, and (d) 900°C.



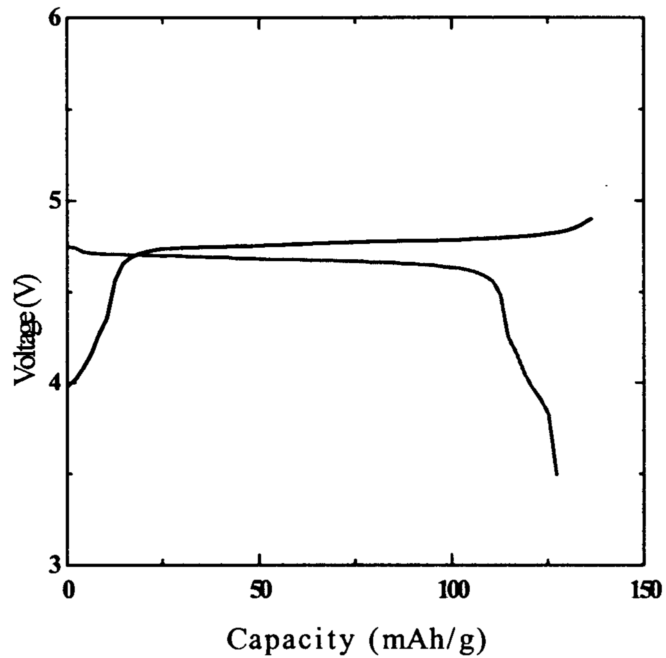
Discharge curves for Li/$LiNi_{0.5}Mn_{1.5}O_4$ cells. (1) Calcined at 850°C and (2) Calcined at 600°C.

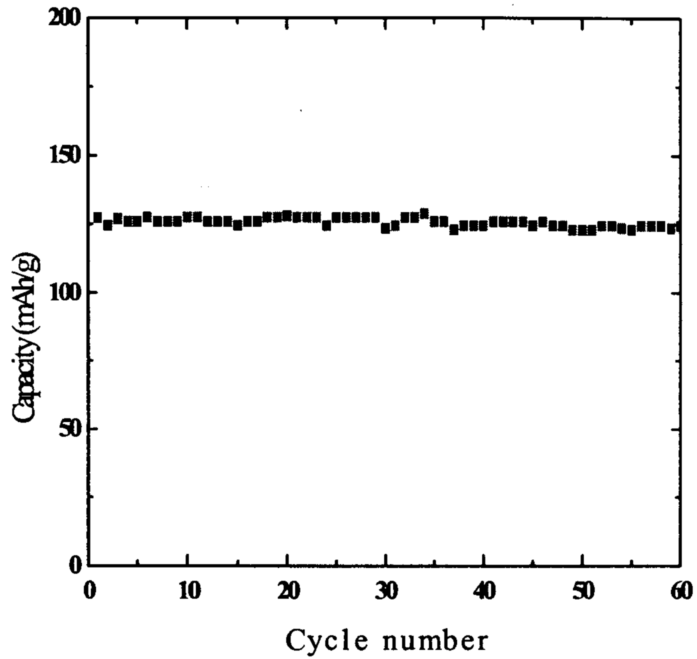


Discharge curves for Li/$LiNi_{0.5}Mn_{1.5}O_4$ cells. (1) Calcined at 850°C and (2) Quenched at 850°C.

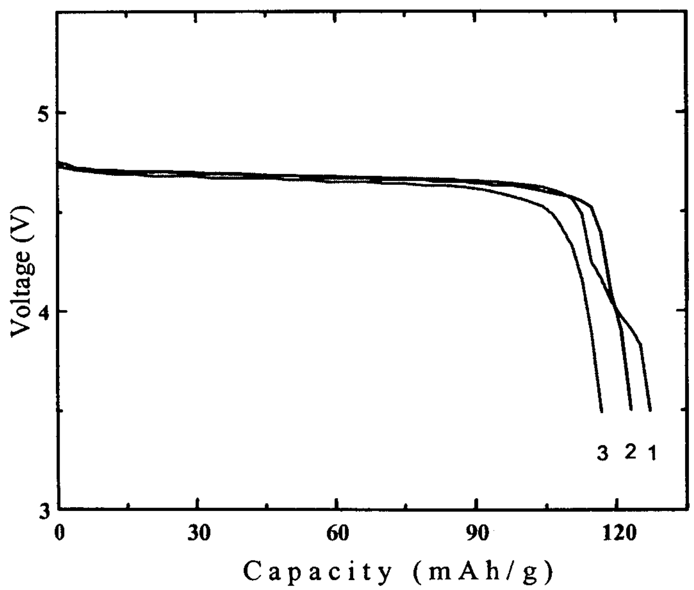


Discharge curves for Li/$LiNi_{0.5}Mn_{1.5}O_4$ cells: (1) 0.25, (2) 0.5, (3) 1.0, (4) 1.5, (5) 2.0 mA/cm^2.

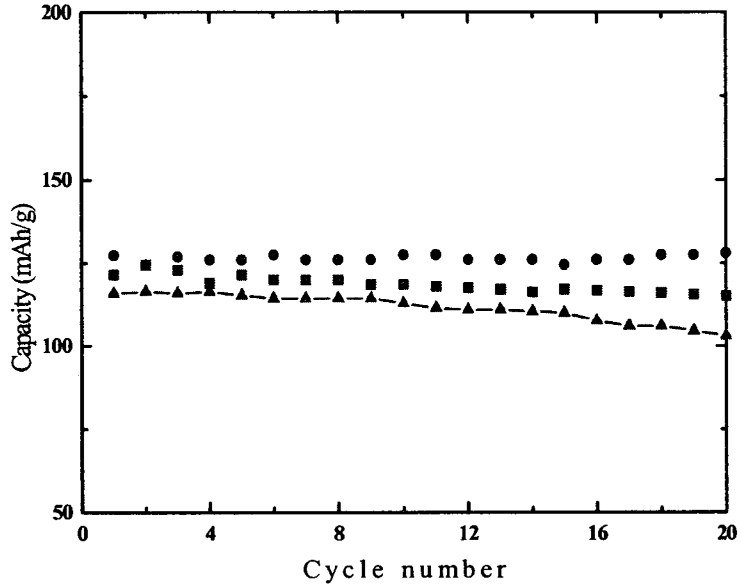




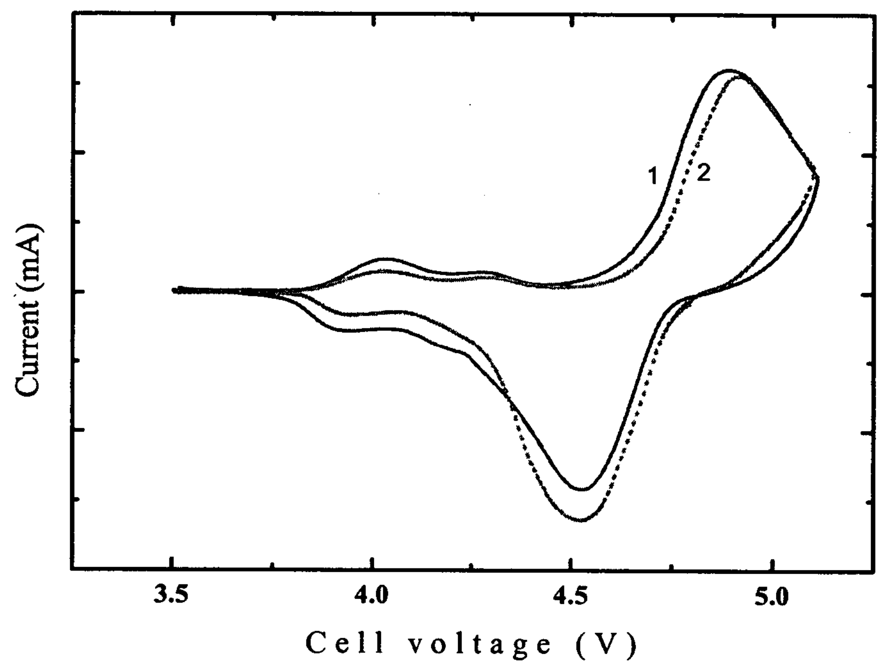
First charge-discharge curve and cycling behavior of $Li/LiNi_{0.5}Mn_{1.5}O_4$ cell in $LiPF_6$ – PC.



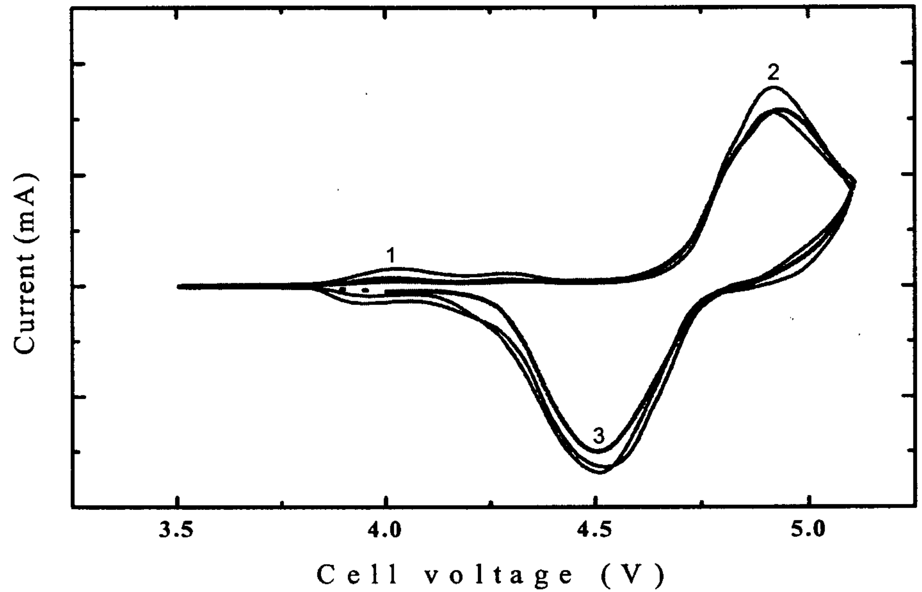
Voltage vs. capacity profiles for (1) Li/$LiNi_{0.5}Mn_{1.5}O_4$, (2) Li/$LiNi_{0.55}Mn_{1.45}O_4$, and (3) Li/$LiNi_{0.6}Mn_{1.4}O_4$.



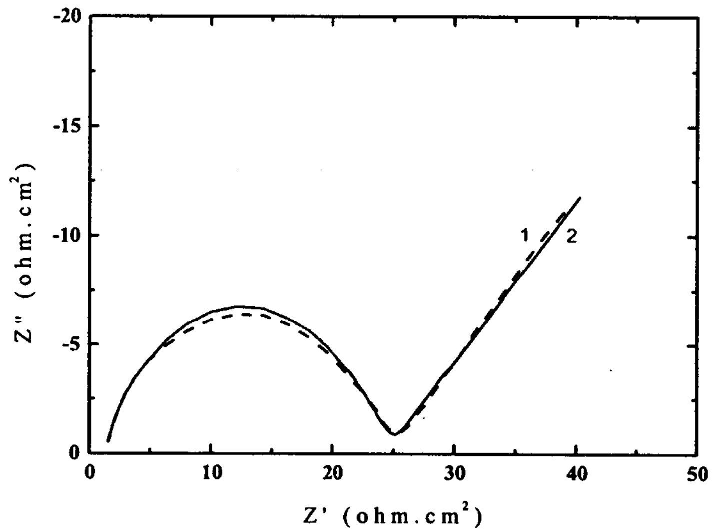
Discharge capacity vs. cycle number for Li/$LiNi_xMn_{2-x}O_4$ cells. Circle for x=0.5, square for x=0.55, and triangle for x=0.6.

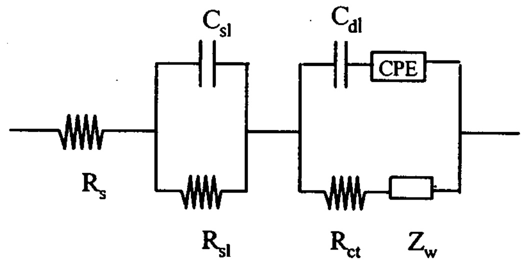


Cyclic voltammograms of $LiNi_{0.5}Mn_{1.5}O_4$ at a rate of 0.05 mV/s. (1) pristine and (2) After thirty cycles.

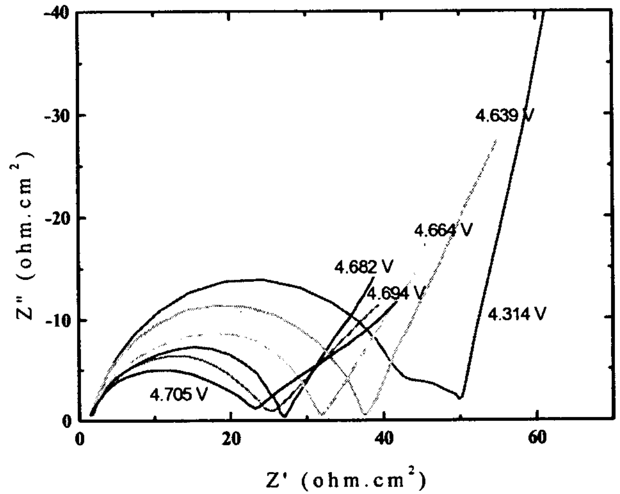


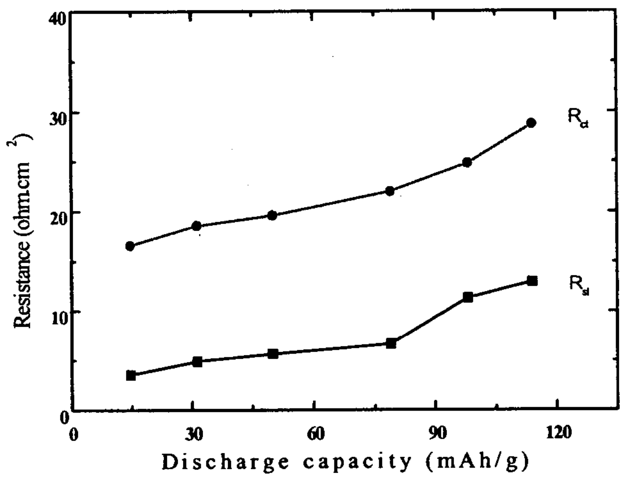
Cyclic voltammograms of electrode (1) $LiNi_{0.5}Mn_{1.5}O_4$, (2) $LiNi_{0.55}Mn_{1.45}O_4$, and (3) $LiNi_{0.6}Mn_{1.4}O_4$ at a rate of 0.05 mV/s.





Equivalent circuit and Nyquist plots of $LiNi_{0.5}Mn_{1.5}O_4$ electrode at the potential, E = 4.705 V.
(1) After the first cycle and (2) After 30 cycles.





Nyquist plots of $LiNi_{0.5}Mn_{1.5}O_4$ electrode obtained at different states of discharge and variation of R_{ct} , C_{dl} as a function of discharge capacity.

Conclusions

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1. Relatively high T results in small surface area particle & O_2 loss
   $LiNi_{0.5}Mn_{1.5}O_4 \rightarrow qLi_zNi_{1-z}O + rLiNi_{0.5-w}Mn_{1.5+w}O_4 + sO_2$ ($\geq 650^{\circ}C$)

2. $LiNi_{0.5}Mn_{1.5}O_4$ material shows a capacity of ~127 mAh/g at 3.5 ~ 4.9 V
   4.65 V plateau due to $Ni^{2+} \rightarrow Ni^{4+}$, while 4.0 V due to $Mn^{3+} \rightarrow Mn^{4+}$
   (> ~124 mAh/g up to 60 cycle)

3. A little excess Ni shows only one plateau at 4.66 V (120 mAh/g)

References

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