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From Discovery to Innovation...

# Influence of Ti Substitution in LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> on Electrochemical Performance and Evaluation of LiNi<sub>0.5</sub>Mn<sub>1.5-x</sub>Ti<sub>x</sub>O<sub>4</sub> (x= 0.05, 0.1) as a Cathode Material

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IMLB 2010 in Montreal, June 28 – July 2, 2010





#### **Outline of Presentation**

- Motivation for this work
- Characterization of near stoichiometric and nickel deficient LiNi<sub>0.5-x</sub>Mn<sub>1.5+x</sub>O<sub>4</sub>
  - Crystallography and morphology
  - Electrochemical performance
- Characterization of LiNi<sub>0.5</sub>Mn<sub>1.5-x</sub>Ti<sub>x</sub>O<sub>4</sub>
  - Crystallography and morphology
  - Electrochemical performance
- Summary and conclusions



#### Motivation for this research

#### • Potential cathode material for zero emission and plug-in hybrid electric vehicles

- Holy grail of higher energy and power densities
- High voltage cathode material of operating at ~ 5V
- Cathode suited to use with  $Li_4Ti_5O_{12}$  for a safer cell with reasonable voltage (>3V)
- Long cycling life
- Simple to prepare
- Low cost
- Environmentally friendly
- Literature data suggested that LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> seemed to meet most of these criteria
  - Cycle life, particularly at high temperatures or charging rates, seemed to be the main unresolved issue [ref. B. Markovsky, Y. Talyossef, G. Salitra, D. Aurbach, H-J. Kim and S. Choi, Electrochem. Comm., 6, 821-826 (2004)]





- Variation of sol-gel method described previously<sup>2,3,4</sup>
- Mn acetate, Ni acetate or Ni nitrate and Li hydroxide dissolved in distilled water, with small amount of carbon black.
- pH adjusted to 9 using ammonium hydroxide
- Mixture stirred for 1 hr at RT, heated at 80°C until viscous gel obtained.
- Gel fired in dry air at 850°C for 12 hrs, annealed at 600°C for 24hrs
  - 2. K. Amine, H. Tukamoto, H. Yasuda & Y. Fujita, Journal of the Electrochemical Society 143, 1607-1612 (1996).
  - 3. X. Wu & S. B. Kim, Journal of Power Sources 109, 53-57 (2002).
  - 4. Q. Zhong, A. Bonakardarpour, M. Zhang, Y. Gao & J. Dahn, Journal of the Electrochemical Society 144, 205-213 (1997).



#### Characterization of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>

- Composition Li<sub>1.08</sub>Ni<sub>0.51</sub>Mn<sub>1.49</sub>O<sub>4.17</sub> by AA analysis – close to stoichiometric
- SEM very distinct crystal facets critical to capacity retention in conventional electrolytes
- Rietveld analysis
  - 88 wt% 'stoichiometric', 9 wt% Nideficient and 3 wt% NiO
  - Excess NiO → over Ni solubility limit
  - ~2% Li on TM site but no TM on Li site in stoichiometric phase
  - Ni oxidation state +2.08



#### Electrochemical evaluation of LiNi<sub>0.5-x</sub>Mn<sub>1.5+x</sub>O<sub>4</sub>



- 4V plateau on charge and discharge disappears when Ni content close to 0.5 – no Mn<sup>3+</sup> present
- Good resolution of Ni<sup>2+</sup> to Ni<sup>3+</sup> and Ni<sup>3+</sup> to Ni<sup>4+</sup> in dQ/dV vs V up to 100 cycles

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#### Electrochemical evaluation of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>



- Galvanostatic cycling between 3.5 4.9 or 4.95V at 88 mA/g (C/2 rate) with conventional electrolyte (1M LiPF<sub>6</sub> in 3:7 EC:DEC) at RT is shown
- Long term cycleability at C/2 rate charge and up to 5C rate discharge at RT
- Capacity retention and coulombic efficiencies decrease at elevated temperatures (60°C)



- Alternative methods of synthesis larger crystals would probably be more stable at high temperatures or high state of charge
- Coatings : oxides of Al, Zr and Bi etc...
- Doping with other elements that might improve the structural and/or electrochemical stability
- It has been suggested that partial substitution of Mn<sup>4+</sup> with Ti<sup>4+</sup> can improve cycle life [ref. R. Alcantara et al, *Chem. Mater.*, **15**, 2376-2382 (2003)]





- 1. Mn acetate, Ni acetate or Ni nitrate, ammonium titanyl oxalate and LiOH dissolved in distilled water, with small amount of carbon black.
- 2.  $pH \rightarrow 10 \text{ using } NH_4OH$
- 3. Mixture stirred for 1 hr at RT, heated at  $80^{\circ}C \rightarrow viscous$  gel obtained.
- 4. Gel fired in dry air @850°C for 12 hrs, annealed @600°C for 24hrs.



### Characterization of LiNi<sub>0.5</sub>Mn<sub>1.5-x</sub>Ti<sub>x</sub>O<sub>4</sub>

- Chemical analysis atomic absorption spectroscopy and XRF
- HR SEM on Hitachi FEG SEM
- Very crystalline distinct crystal facets visible





LiNi<sub>0.5</sub>Mn<sub>1.4</sub>Ti<sub>0.1</sub>O<sub>4</sub>



#### XRD characterization of LiNi<sub>0.5</sub>Mn<sub>1.5-x</sub>Ti<sub>x</sub>O<sub>4</sub>

- XRD Bruker-AXS D8 diffractometer using Cu Kα or Cr Kα radiation.
- Minor impurity of a Ni-rich oxide which is probably Ni<sub>6</sub>MnO<sub>8</sub> is evident in XRD
- No evidence in Rietveld analysis of ordered P4<sub>3</sub>32 structure – spinel phases appear to be disordered Fd-3m structure



#### XRD characterization of LiNi<sub>0.5</sub>Mn<sub>1.5-x</sub>Ti<sub>x</sub>O<sub>4</sub>



- Since Cu Kα is highly absorbed and poorly scattered by Mn, Cr Kα (2.29 Å) was used for the more detailed XRD analysis
- All samples had small amount of Ni-rich oxide, which is probably Ni<sub>6</sub>MnO<sub>8</sub>
- Lattice parameters increase linearly with increasing Ti content (x)

#### Voltage Profile of LiNi<sub>0.5</sub>Mn<sub>1.4</sub>Ti<sub>0.1</sub>O<sub>4</sub>



Capacity (mAh /g)

•Substitution with 0.1 Ti increases capacity (red curve)

- •No redox activity at ~4 V due to absence of Mn<sup>3+</sup>
- Irreversible capacity loss higher on first cycle than for undoped LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>



### Electrochemical evaluation of LiNi<sub>0.5</sub>Mn<sub>1.4</sub>Ti<sub>0.1</sub>O<sub>4</sub>



- Good capacity retention to > 500 cycles with little change in voltage profile or capacity after the 100th cycle.
- Notable change in dQ/dV vs V plot from  $1^{st}$  cycle to later ones may be indicative of a formation reaction occurring on  $1^{st}$  cycle note discharge voltage
- Clear resolution of the  $Ni^{2+}$  to  $Ni^{3+}$  and  $Ni^{3+}$  to  $Ni^{4+}$  steps in dQ/dV vs V plot

### $Li//LiNi_{0.5}Mn_{1.5-x}Ti_{x}O_{4}$ (x= 0.05,0.1)



- On galvanostatic cycling, capacity decreases at higher rates
- At x =0.05 Ti, the capacity is lower than for x= 0.1
- Capacity retention is quite good after some loss on early cycling

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# AC impedance on Li// LiNi<sub>0.5</sub>Mn<sub>1.4</sub>Ti<sub>0.1</sub>O<sub>4</sub>



- Impedance at end of charge (4.8 V): filled symbols
- Impedance at end of discharge (3.8V): open symbols
- Impedance it greater at the end of discharge (EOD) than at the end of charge (EOC)
- At 60°C, impedance at both EOC and EOD increase on cycling
- At RT, impedance at EOC is stable after 1<sup>st</sup> cycle, but decreased on EOD with cycling
- After a few cycles, the impedance is greater at 60 °C than at RT

### Longer term cycling – Li//LiNi<sub>0.5</sub>Mn<sub>1.4</sub>Ti<sub>0.1</sub>O<sub>4</sub> at 60°C



- At 60°C, electrolyte solvents have a large impact on cycle life
- Electrolytes with EC:DMC have much better capacity retention than ones with EC:DEC
- Pre-conditioning by cycling at RT seems to improve performance



# $Li//LiNi_{0.5}Mn_{1.4}Ti_{0.1}O_4$ with EC/DMC or EC/DEC



 Choice of electrolyte solvent affects rate performance and coulombic effiency

• Electrolyte with EC:DMC performs better at 60°C than does EC:DEC



# $Li_4Ti_5O_{12} //LiNi_{0.5}Mn_{1.4}Ti_{0.1}O_4$



- However the capacity of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>//LiNi<sub>0.5</sub>Mn<sub>1.4</sub>Ti<sub>0.1</sub>O<sub>4</sub> cells degrade if charged to voltages > 3.5V
- Plateau above 3.5V is evidence of electrolyte decomposition

- Combining  $LiNi_{0.5}Mn_{1.4}Ti_{0.1}O_4$  with  $Li_4Ti_5O_{12}$ provides a cell with > 3V output
- Improved safety characteristics



#### Longer term cycling Li //LiNi<sub>0.5</sub>Mn<sub>1.4</sub>Ti<sub>0.1</sub>O<sub>4</sub>



- Very good capacity retention to > 1500 cycles with 0.65C (88mA/g) charge and up to 5 C (675 mA/g) discharge
- CC-CV cycling did not seem to offer much improvement

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- Good capacity, capacity retention and coulombic efficencies can be achieved with both LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and LiNi<sub>0.5</sub>Mn<sub>1.4</sub>Ti<sub>0.1</sub>O<sub>4</sub> using quite conventional electrolyte formulations at RT.
- Long term galvanostatic cycling at high discharge rates is possible in coin cells as long as the charging rate is low enough to prevent gassing.
- Unfortunately, partial substitution of Mn with Ti does not resolve the problems the electrochemical performance with conventional electrolytes at elevated temperatures.
- However, careful choice of electrolyte formulation does improve the high temperature performance.





This work was partially supported by Natural Resources Canada's Program on Energy R&D through the Clean Transportation Systems Portfolio. The authors gratefully acknowledge financial support from Defence R&D Canada.



#### Thank you for your kind attention

