NEW CATHODE MATERIALS

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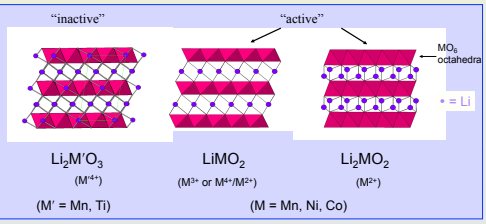
MENU | Composite Mn(IV)-Based Oxides | Mn-Spinel Oxides | Coatings ♪

APPROACH: To develop safe manganese-oxide based electrodes for Li-ion batteries

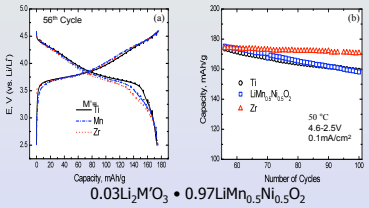
- High energy/capacity class – Mn layered oxide structures with rock salt domains (i.e. composite electrode design)
- High power class – Mn high-voltage spinel structures
- High-performance protective coatings to improve properties of cathode interface



Themes♪

- *Ni(II) and Mn(IV) redox combination* in layered and spinel oxides provides stability & maximizes capacity
  - ✓examples: $Li[Ni_{0.5}Mn_{0.5}]O_2$, $Li[Ni_{0.5}Mn_{1.5}]O_4$
- *Composite electrode design* - Addition of rock salt components/domains ($Li_2M'O_3$) stabilizes layered oxides (see structural relationships). Existence of rock-salt domains promotes Ni site immobility and invariance, thereby enhancing stability & electrochemistry.
  - ✓Li in Li_2MnO_3 domains can provide Li source and Li conduction pathways in layered phase
  - ✓Li_2MnO_3-> role of layered "MnO_2" interconversion
- *Coatings* - modifying cathode interface
  - ✓examples (a) surface current distribution, (b) wettability of electrode/electrolyte interface, and (c) amphoteric scavenger of electrolyte impurities

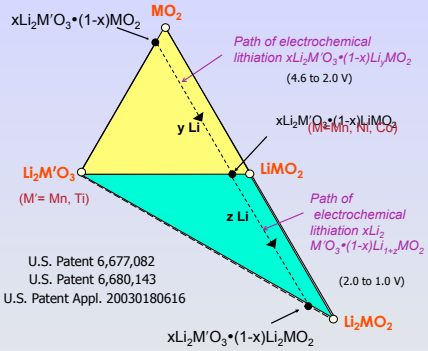
High energy...♪



$0.03Li_2M'O_3 \bullet 0.97LiMn_{0.5}Ni_{0.5}O_2$

- *Stablized Mn(IV) layered phase yields 170 mAh/g at 50 °C (100 cycles)♪*
- *Recent optimized compositions have ♪ yielded 200 mAh/g at room temperature♪ ♪*

Rock-salt/Layered Structural Composition Relationships



U.S. Patent 6,677,082
U.S. Patent 6,680,143
U.S. Patent Appl. 20030180616

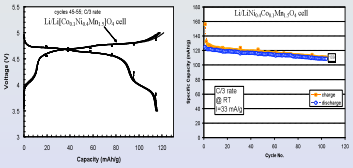
Induced Electroactivity of Li_2MnO_3♪

- First charge irreversible capacity proportional to Li_2MnO_3 content in composite electrode
  - ➢Li_2MnO_3 electroactive at 4.5 V
- Capacity loss on first charge – mechanism
  1. $Li_2MnO_3 \longrightarrow 2\ Li^+ + [Mn^{4+}O_3]^{4-} + 2\ e^-$
  2. $[Mn^{4+}O_3]^{4-} \longrightarrow MnO_2 + \frac{1}{2}\ O_2$

rxn.1 – theoretical capacity 459 mAh/g (electrochemical extraction reaction)

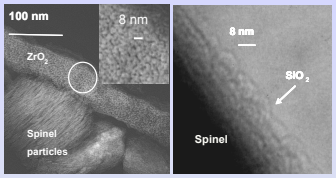
rxn. 2 - layered MnO_2 formed is structurally integrated into $LiMO_2$ framework (chemical loss of O_2 with subsequent reaction with electrolyte)

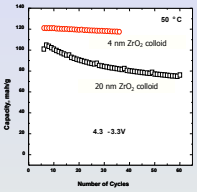
High power...♪



- *Cobalt stabilized 5 V spinel enhances ♪ cyclability♪*
- *Spinel series $Li[Ni_{0.5-x}Co_xMn_{1.5}]O_4$ ($0 \le x \le 0.5$) synthesized, characterized and tested♪*
- ***Material milestone of ♪ 110 mAh/g (100 cycles)♪***

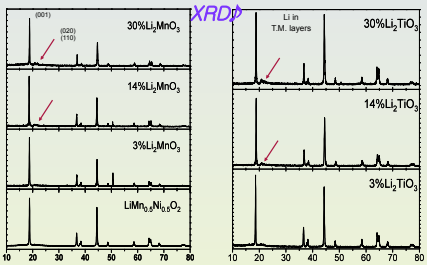
Coatings...♪





- *Nanoparticulate size and fusion/ reaction to base oxide are key factors influencing electrode performance♪*

Structures♪



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- *Short-range Ni-Mn/Ti order, scrambling, ♪ segregation and domain formation♪*

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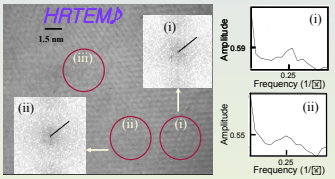
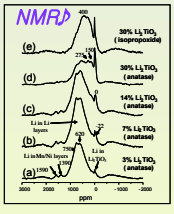
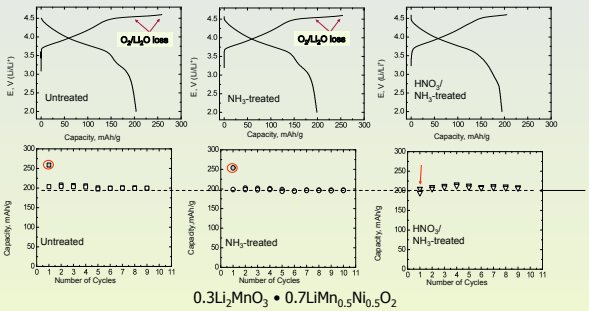
COMPLICATED INTER-RELATED PHASES : SYNTHESIS DEPENDENT PROPERTIES♪





Current and future studies...♪



$0.3Li_2MnO_3 \bullet 0.7LiMn_{0.5}Ni_{0.5}O_2$

- *Mn(IV) composite treated in order to remove irreversible voltage plateau♪*
- *Reduced irreversible capacity loss at 4.5 V (to 10-15%) – with no loss in discharge capacity♪*
- ***Irreversible capacity significantly lowered♪***
- *Optimization of composite (layered) and spinel electrodes to be a major focus in FY05♪*

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