Advanced Cathode Materials

Christopher S. Johnson and Michael M. Thackeray

Electrochemical Technology Program, Chemical Engineering Division, Argonne National Laboratory

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

MOTIVATION: To develop manganese-oxide based electrodes for Li-ion batteries in consumer and transportation applications

- 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

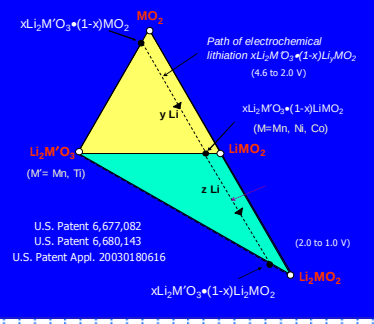
Mn-based electrodes can meet safety, cost, and abundance targets necessary for the transportation market of EVs and HEVs

CHALLENGE: Mn-based oxides typically suffer from phase changes and dissolution problems during cycling in a lithium battery

- Composite design stabilizes the phase structure of the electrode material. For example, the cathode in alkaline batteries is a composite γ-MnO_2 structure that is successfully used in millions of commercial cells. We are using a similar approach to the design of cathodes for lithium batteries
- Coatings are being developed to enhance stability of electrode/electrolyte interface, and improve interfacial electrode kinetics

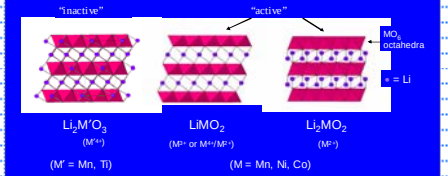
OUR APPROACH

Compositional Phase Diagram



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

STRUCTURES



- Layered structures are closely related; Li_2MnO_3 phase is interconnected or intergrown into active phases such as $LiCoO_2$ or $Li(NiMnCo)_{1/3}O_2$

Themes

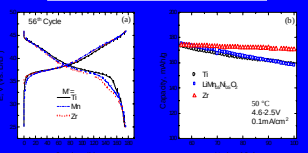
- ***Ni(II) and Mn(IV) redox combination*** **in layered and spinel oxides provides stability and maximizes capacity.**
  - ✓ **Examples: $Li[Ni_{0.5}Mn_{0.5}]O_2$, $Li[Ni_{0.5}Mn_{1.5}]O_4$**
- ***Composite electrode design*** **- Addition of rock salt components/domains ($Li_2M'O_3$) stabilizes layered oxides (see structural relationships). Existence of rock-salt domains promotes Ni site immobility and invariance, thereby enhancing stability and 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**

CONCLUSIONS

- Composites of Mn-based oxides for cathodes in next-generation Li-ion batteries hold much promise for improved cycling performance and stability
  - ➢ Layered-layered and layered-spinel composites offer tailored features of high energy and/or high power for an end- application-based designed battery
- Coatings for composites will further improve interface of cathodes and boost electrochemical capabilities such as interfacial kinetics, or greater resistance to corrosion

KEY ENABLING TECHNOLOGY DRIVERS UNDER DEVELOPMENT

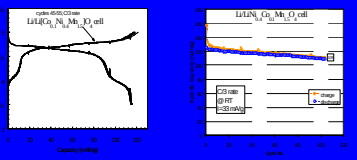
High energy...



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

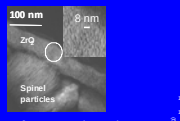
- *Stablized Mn(IV) layered phase yields 170 mAh/g at 50 °C (100 cycles)*
- *Recent optimized compositions have yielded 200 mAh/g at room temperature*

High power...



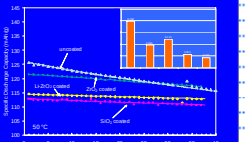
- *Cobalt stabilized 5 V spinel enhances cyclability*
- *Spinel series $Li[Ni_{0.5-x}Co_xMn_{1.5}]O_4$ ($0 \leq x \leq 0.5$) synthesized, characterized and tested*

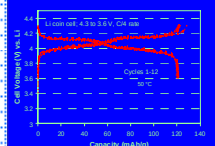
Coatings...



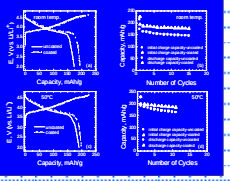
TEM of microtomed particle

ZrO_2-coated $LiMn_2O_4$ electrodes show improvement in cycling stability at 50 °C





Voltage profile of ZrO_2-coated $LiMn_2O_4$ spinel electrode



ZrO_2-coated $LiMn_{0.5}Ni_{0.5}O_2$ electrodes show enhanced cycling stability

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