Argonne NATIONAL LABORATORY

Advanced Cathode Materials for High-Power Applications

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INTRODUCTION

- **Hybrid Electric Vehicles (HEVs)**
  - Internal combustion engine (ICE) combined with electric motor driven by batteries
  - Advantages
    - *Higher fuel efficiency (i.e., higher gas mileage) and improved power*
    - *Less emission*
  - Most of the current hybrid cars adopt NiMH batteries to drive the electric motor.
- **Li-ion vs. NiMH**
  - Advantages: *Higher power/energy density and lower self-discharge rate*
  - Barriers: *Calendar life, abuse tolerance, and cell cost*
- **Cathode material plays significant role in the life and safety of high power lithium batteries**
  - Argonne, under the DOE's Advanced Technology Development Program (ATD), has identified that the cathode material plays a major role in the calendar life of lithium ion batteries
  - Cathode materials requirements for HEV batteries
    - *Excellent power capability, low and stable impedance during battery operation, good thermal safety characteristics, and low cost*
    - *$LiNi_{1/2}Mn_{1/2}O_2$ has shown very stable capacity and impedance after extensive cycling and could meet the calendar life and safety requirements*

$Li(Ni_{0.5}Mn_{0.5})O_2$

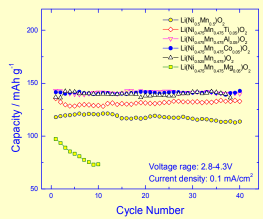
- **Layered α-$NaFeO_2$ structure as $LiCoO_2$ and $LiNiO_2$**
- **Pros and cons of $Li(Ni_{0.5}Mn_{0.5})O_2$**
  - Pros
    - *Cost advantage due to the absence of Co and low Ni content*
    - *Much better calendar and cycle life than other layered oxides*
    - *Low thermal reactivity due to the low Ni-content and the stabilizing effect of the large amount of Mn-ions in the structure.*
  - Cons
    - *Materials prepared by conventional methods show poor rate and low power capabilities*

AIMS OF THIS WORK

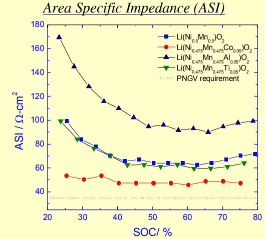
- **Improve the rate and power characteristics of $Li(Ni_{0.5}Mn_{0.5})O_2$ through various strategies**
  - Cation doping
  - Control of Li content
  - New synthesis processes
- **Investigate the effect of various dopants and Li content on the electrochemical properties, impedance, and thermal safety**
- **Explore the use of $Li(Ni_{0.5}Mn_{0.5})O_2$ as cathode materials for high-power Li-ion batteries**

EFFECTS OF CATION DOPANTS – $Li(Ni_{0.5-x}Mn_{0.5-x}M'_{2x})O_2$

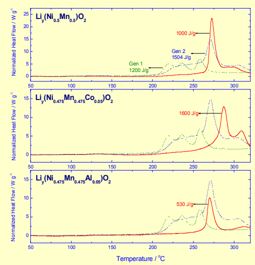
Cycling Performance



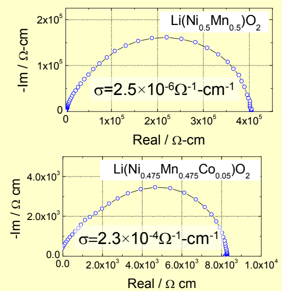
Area Specific Impedance (ASI)



Differential Scanning Calorimetry



Electronic Conductivity Measurement



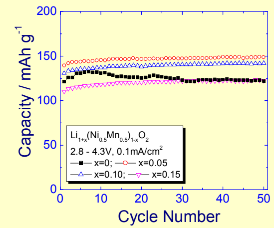
- The cation-doped $Li(Ni_{0.5}Mn_{0.5})O_2$ showed good cycling stability with higher capacity than the undoped one.
- The 5 mole% Co doping lowered the impedance significantly by increasing the electrical conductivity of $Li(Ni_{0.5}Mn_{0.5})O_2$.
- The $Li(Ni_{0.5}Mn_{0.5})O_2$-based cathode materials exhibited better thermal safety characteristics than $Li(Ni_{0.8}Co_{0.2})O_2$-based materials.

SUMMARY

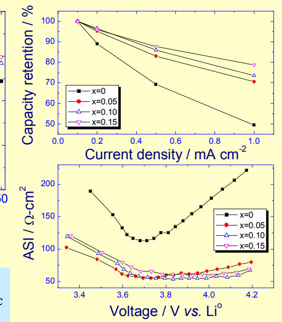
- To enhance the electrochemical properties of $Li(Ni_{0.5}Mn_{0.5})O_2$, especially to lower the cell impedance, various doping strategies have been carried out.
  - Cation doping: 5 mole % Co in the transition metal site increased capacity and reduced impedance.
  - Li content: 5-10 mole % excess Li showed increased capacity, lowered impedance, and improved rate capability.
  - Through the use of a new Argonne proprietary process, the $Li(Ni_{0.5}Mn_{0.5})O_2$/Li cell was able to achieve 80% capacity retention at 9C rate
- It is anticipated that a combinatorial approach to find optimum Co and Li contents combined with the new Argonne process could further increase the rate and power capability of this cathode material and make it suitable for batteries for HEV applications.

EFFECTS OF LITHIUM CONTENT – $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$

Cycling Performance



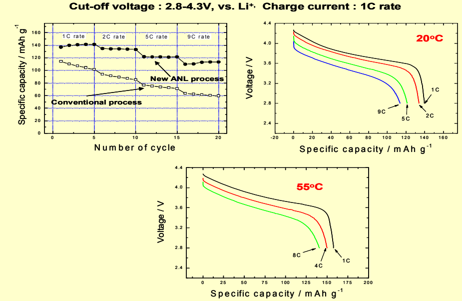
Rate Capability and Area Specific Impedance (ASI)



- The Li content significantly affected the capacity, rate capability, and area specific impedance.
- The Li-excess $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$ materials exhibit improved rate capability and lower area specific impedance.
  - Enhanced electronic conductivity due to Ni^{3+} by Li incorporation into the metal layer.
  - Improved Li diffusivity due to less cation disorder (i.e., fewer Ni ions in the lithium layer), which was confirmed by the refinement of XRD patterns.

Significant rate improvement in $LiNi_{1/2}Mn_{1/2}O_2$ using a new Argonne proprietary process

Cut-off voltage : 2.8-4.3V, vs. Li$^+$, Charge current : 1C rate



- Argonne's new preparation process has led to a significant increase in the rate performance of $LiNi_{1/2}Mn_{1/2}O_2$ (rate capability better than the one reported recently by MIT using ion exchange)
- The new Argonne process can be easily scalable

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