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Developing new high energy gradient concentration cathode material

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Argonne National Laboratory

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UChicago ▶ Argonne LLC

Office of Science U.S. DEPARTMENT OF ENERGY

A U.S. Department of Energy laboratory managed by UChicago Argonne, LLC

Project ID:esp_10_amine

Overview

Timeline

- Start - October 1st, 2008.
- Finish - September 30, 2009.
- 40%

Barriers

- Barriers addressed
  - Very high energy
  - Long calendar and cycle life
  - Excellent abuse tolerance

Budget

- Total project funding
  - DOE share: 200K

Partners

- Interactions/ collaborations:

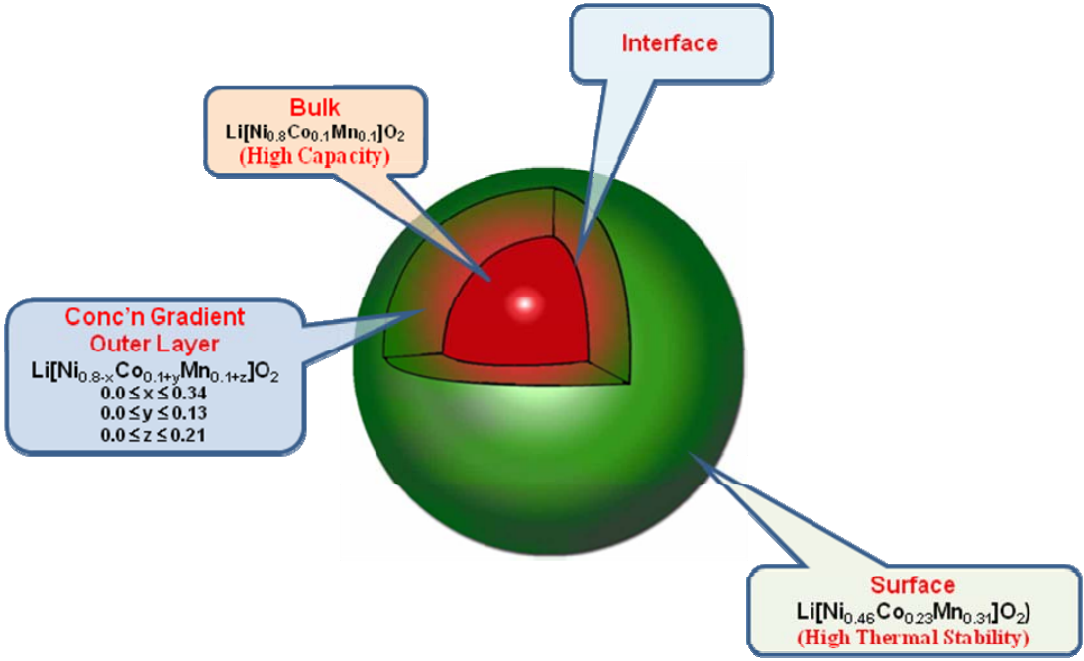
  Prof. Y.K. Sun (Hanyang University)
- Project lead: Khalil Amine

Objectives of the work

- Develop a new high energy cathode material for PHEV applications that provides:
  - Over 200mAh/g capacity
  - Good rate capability
  - Excellent cycle and calendar life
  - Good abuse tolerance

Approaches for Developing High energy cathode material

Develop a novel high-capacity and safe cathode material, in which each particle consists of bulk material $Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$, that provide over 200mAh/g capacity, surrounded by a concentration-gradient outer layer where nickel ions are gradually replaced with manganese ions to provide outstanding cycle life and safety. The resulting surface composition is $Li[Ni_{0.46}Co_{0.23}Mn_{0.31}]O_2$, which is much more stable in contact with the electrolyte than is the bulk composition.



FY 2009 plans & schedule

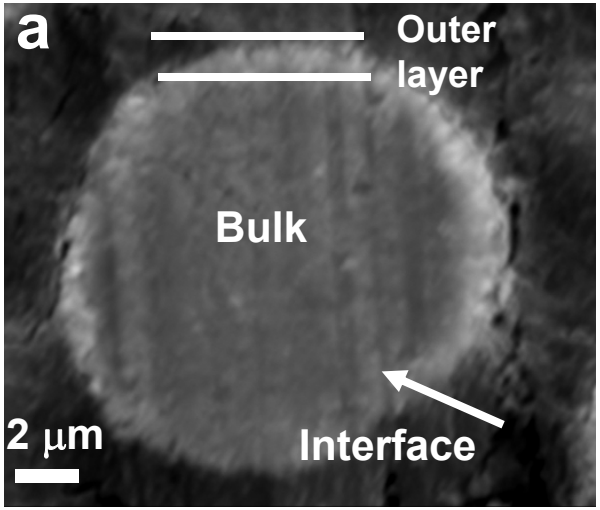
- Develop a new process that provide a Ni-Mn-Co- Hydroxide precursors having gradient concentration (Sep 2009)
- Proof of concept of high energy concentration gradient cathode material in small quantities (Sep 2009)
- Demonstrate the high capacity of concentration gradient material (Sep 2009)
- Demonstrate the good cycle life of the high capacity gradient concentration (Sep 2009)
- Demonstrate the improvement in the safety characteristics using DSC of the gradient concentration material (Sep 2009)

Recent Accomplishments and Progress

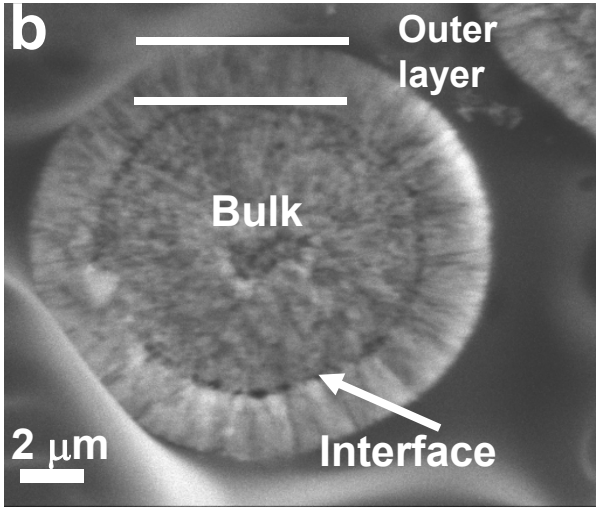
- Was able to initially develop a co-precipitation process that provide small quantities of a high energy gradient concentration precursor and cathode material.
- Was able to characterize the material and demonstrate that the material have a gradient concentration with changing concentration of Ni, Mn and Co within each particle.
- Was able to demonstrate that the gradient concentration cathode material provides high capacity, good cycle life and excellent abuse tolerance.

Scanning electron microscopy (SEM) of a cross section of precursor hydroxide and the final lithiated cathode oxide having concentration gradient

precursor hydroxide

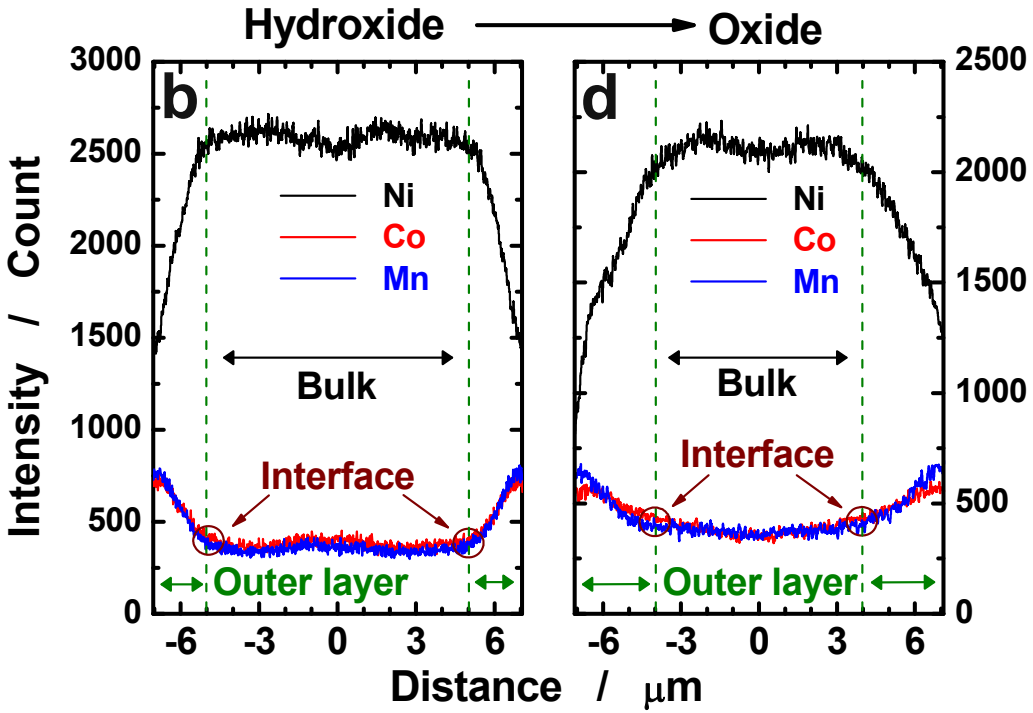


lithiated oxide



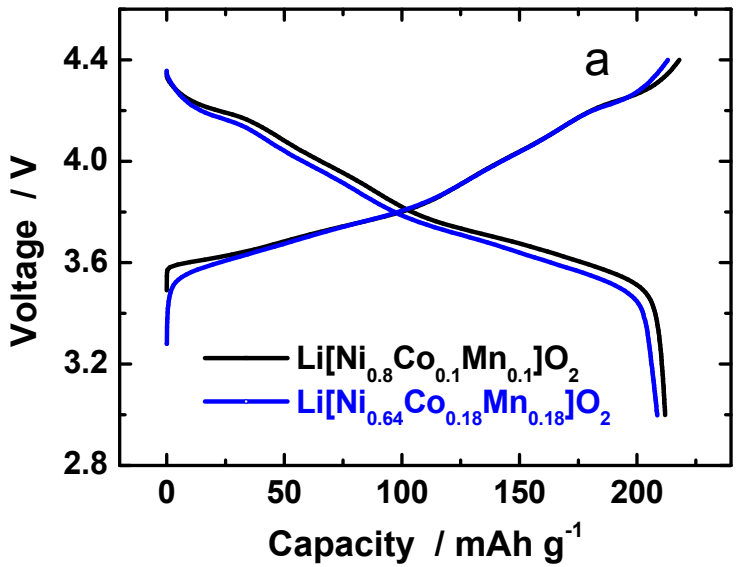
Lithiated oxide shows clearly the bulk material (about 8 μm diameter), the interface were the compositional changes started and a uniform outer layer were Ni-decreases gradually and Mn-increases gradually as the surface of the particle approaches. This new concept will limit any possible separation between the bulk and the outer layer.

Electron-probe X-ray micro-analysis (EPMA) results of precursor hydroxide and the final lithiated oxide



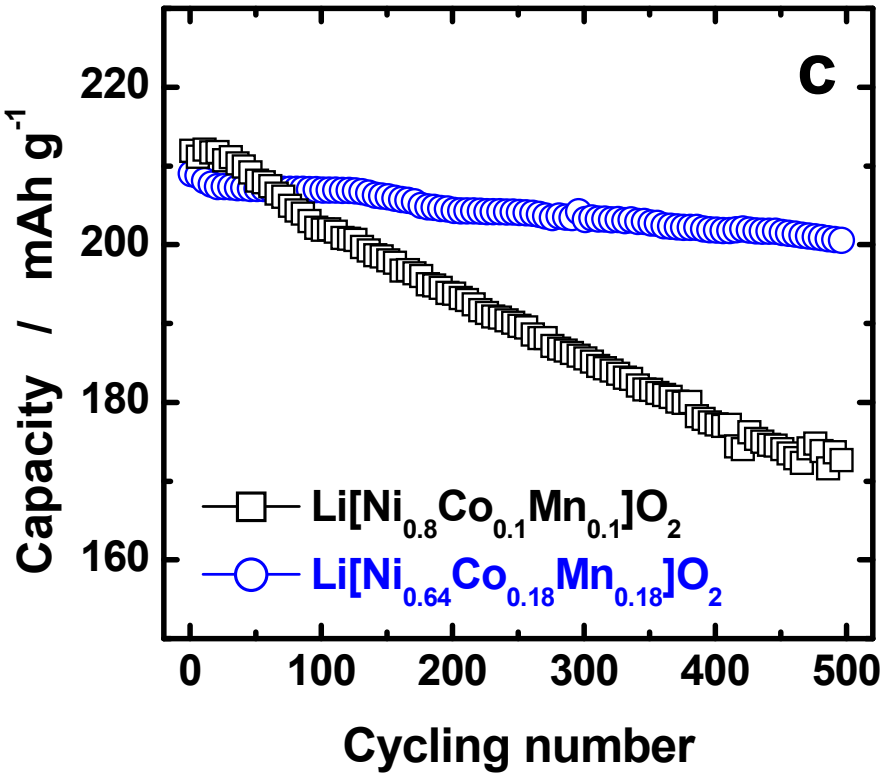
Electron-probe X-ray micro-analysis of precursor and final lithiated oxide shows that the nickel rich bulk has a thickness of 8 μm with stable Ni, Mn, and Co composition and the outer layer thickness is 2 μm were the Ni concentration decreased sharply and the Mn and Co concentration increased toward the surface of the particle

Initial Charge and Discharge of gradient concentration material with average composition $LiNi_{0.64}Co_{0.18}Mn_{0.18}O_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ reference



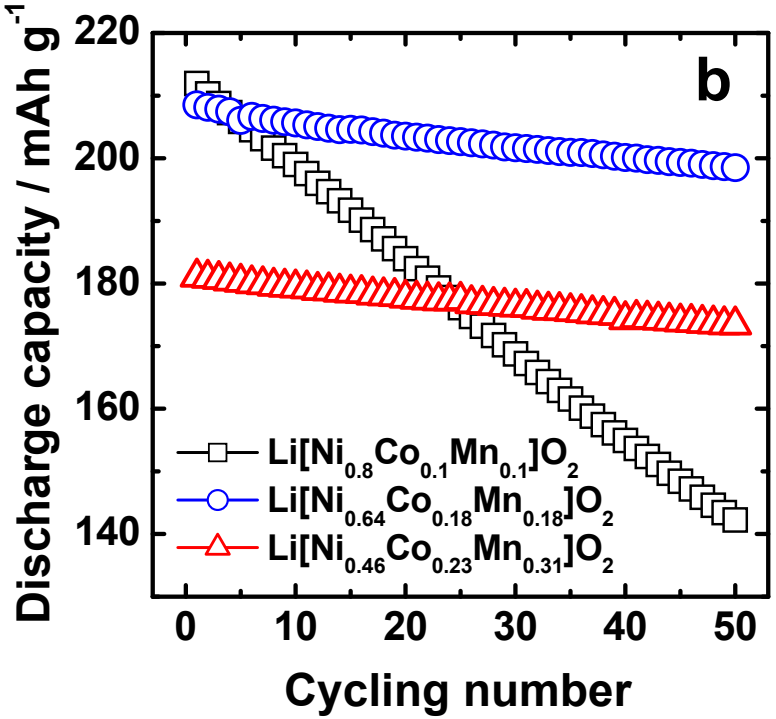
Discharge capacity of gradient concentration material with average composition $LiNi_{0.64}Co_{0.18}Mn_{0.18}O_2$ is almost similar to that of the bulk material $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (about 209mAh/g at 1C rate)

Comparison of cycling performance of gradient concentration material with average composition $LiNi_{0.64}Co_{0.18}Mn_{0.18}O_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ reference



New gradient concentration cathode material with average composition $LiNi_{0.64}Co_{0.18}Mn_{0.18}O_2$ shows excellent cycling performance at 4.4V and 25°C compared to the the bulk material $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$

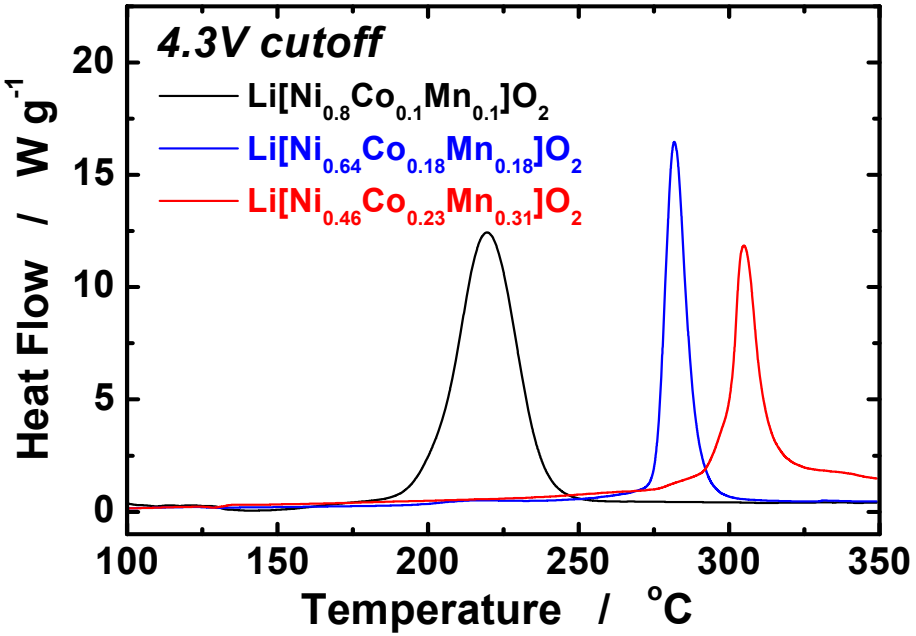
Comparison of cycling performance of gradient concentration material ($LiNi_{0.64}Co_{0.18}Mn_{0.18}O_2$), $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (bulk composition) and $LiNi_{0.46}Co_{0.23}Mn_{0.31}O_2$ (outer surface composition)



✓New gradient concentration cathode material with average composition $LiNi_{0.64}Co_{0.18}Mn_{0.18}O_2$ shows excellent cycling performance at 4.4V and 55°C compared to the bulk material $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$.

✓Material that have the same composition as the outer layer composition of the new gradient concentration shows similar capacity retention but lower discharge capacity than the gradient concentration

Comparison of safety performance using DSC of gradient concentration material ($LiNi_{0.64}Co_{0.18}Mn_{0.18}O_2$) $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (bulk composition) and $LiNi_{0.46}Co_{0.23}Mn_{0.31}O_2$ outer surface composition)



✓New gradient concentration cathode material with average composition $LiNi_{0.64}Co_{0.18}Mn_{0.18}O_2$ shows excellent safety characteristics compared to the the bulk material $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$.

✓Material that have the same composition as the outer layer composition of the new Gradient concentration material shows slightly better safety performance than the gradient concentration

Summary

•New gradient concentration cathode material with very high capacity was developed in collaboration with Prof. Sun of Hanyang University.

•Cross section SEM and EPMA shows that each particle of the material has a bulk composition of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ to provide high energy and an outer layer rich in Mn to provide high stability *vs.* the electrolyte.

•Gradient concentration material shows 209 mAh/g at 1 C rate when charged to 4.4V.

•Gradient concentration material shows excellent cycling performance at 55^{o}C, 4.4V and 1C rate.

• Safety performance of gradient concentration material is excellent when compared to the bulk material.

Future work

•Tune the synthetic process to obtain highly pure gradient concentration material in 100g quantities to carry out extensive characterization and testing.

•Further optimize the composition of the outer layer of the gradient concentration to maximize the surface stability of the material.

•Further optimize the thickness of the outer layer of the gradient concentration to a minimum possible to further increase capacity while maintaining good surface stability.

•Carry out calendar and cycle life test of optimum gradient concentration material.

•Carry out extensive safety test including ARC test and overcharge test.

• investigate the process of scaling up the optimum gradient concentration cathode material for potential use in the high energy cylindrical cells.

Future work

•Carry out extensive safety test including ARC test and overcharge test.

• investigate the process of scaling up the optimum gradient concentration cathode material for potential use in the high energy cylindrical cells.

•Investigating the nano-coating of the material with metal fluoride , phosphate and oxide to reduce stabilize the gradient concentration cathode interface in order to improve the cycle life at elevated temperature (2010)