Advanced Nano-Composite Lithium-Metal-Oxide Electrodes for High Energy Lithium-Ion Batteries

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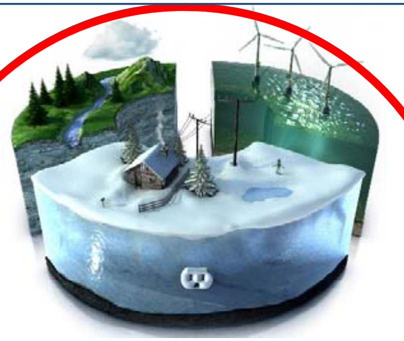
The 7th US-Korea Forum on Nanotechnology: Nanomaterials and Systems for Nano Energy
Seoul, Korea, April 5-6, 2010

Diverse Applications of Li-ion Batteries

e.g.,SoCalEdison-A123
32 MWh LIB

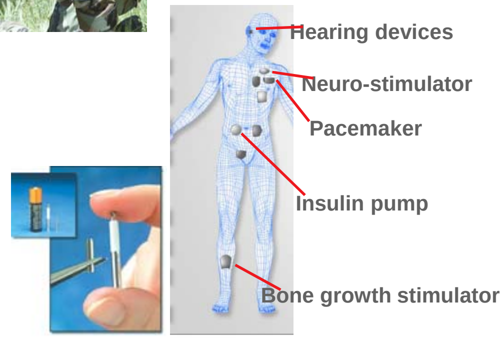


Smart Grid
(Utility-scale energy storage)

Consumer Electronics

Military Applications

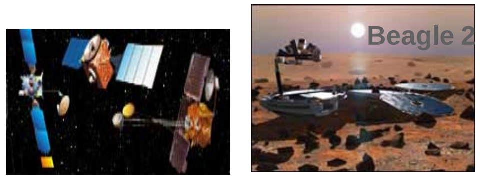
Li-ion Batteries as power sources



Medical Devices

Miscellaneous
(power tools, backup power, etc.)

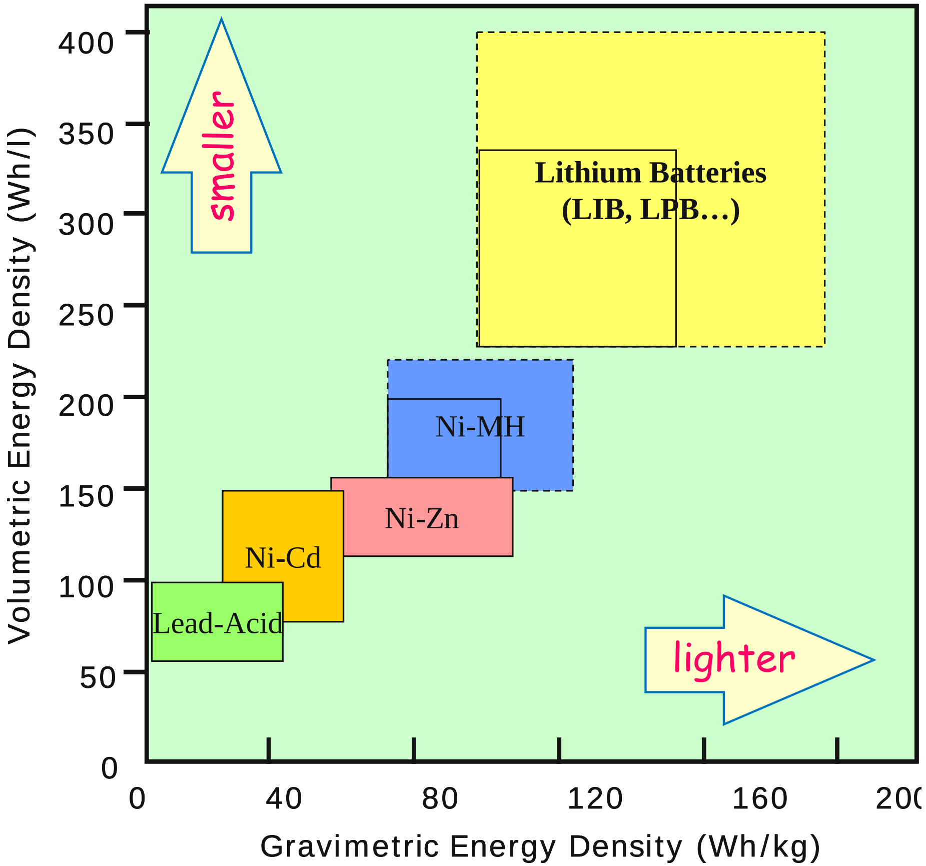
Transportation

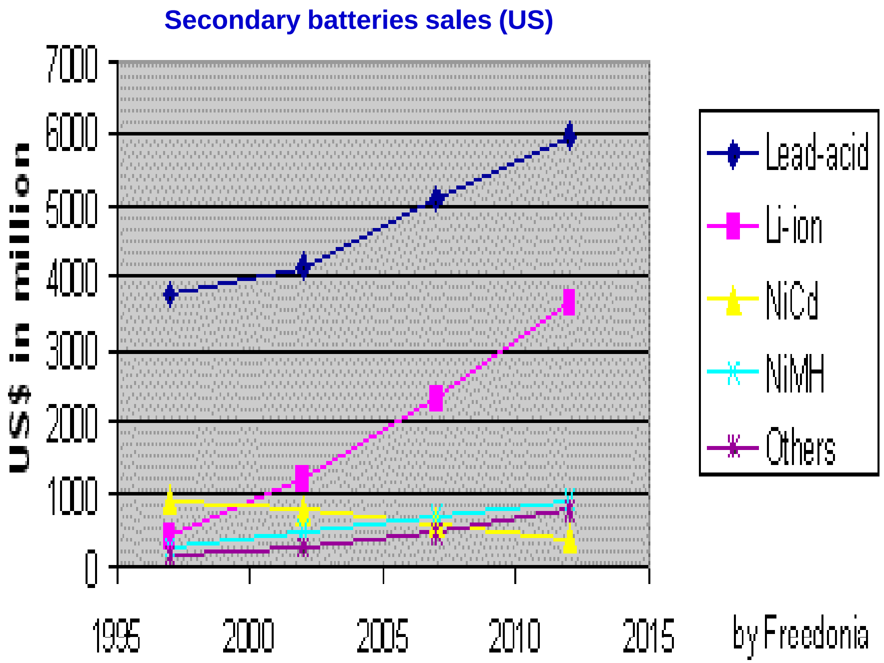


Spaceships and Satellites

e.g.,HEV, PHEV, EV, E-Bike

Why Li-ion Batteries?





- Li-ion battery is the battery chemistry of choice for future generations of energy storage systems for portable electronics, power tools, and electric vehicles. LIB is also one of the candidates for utility-scale electric energy storage systems.

LIB as Energy/Power Source for Transportation

- Plug-in Hybrid Electric Vehicles (PHEV)
  - A hybrid vehicle with batteries that can be recharged by connecting a plug to an electric power source (or by ICE, if necessary): all electric range of 10+ miles (current target: 40+ miles)
  - Impact on Energy, Economy, and Environmental Issues
    - About half the gasoline consumed in the U.S. is consumed in the first 20 miles of daily travel of an automobile.
    - Therefore, PHEV can significantly reduce foreign oil dependence as well as toxic and greenhouse gas emission
    - President Obama's speech to congress (24 Feb 2009): "We know the country that harnesses the power of clean, renewable energy will lead the 21st century. … New plug-in hybrids roll off our assembly lines, but they will run on batteries made in Korea."
    - Significant, nation-wide investment is being made by US (federal and state) government and commercial sectors for R&D activity as well as for establishing manufacturing industry (job creation)

DOE Targets for Energy Storage Systems for HEVs, PHEVs, and EVs

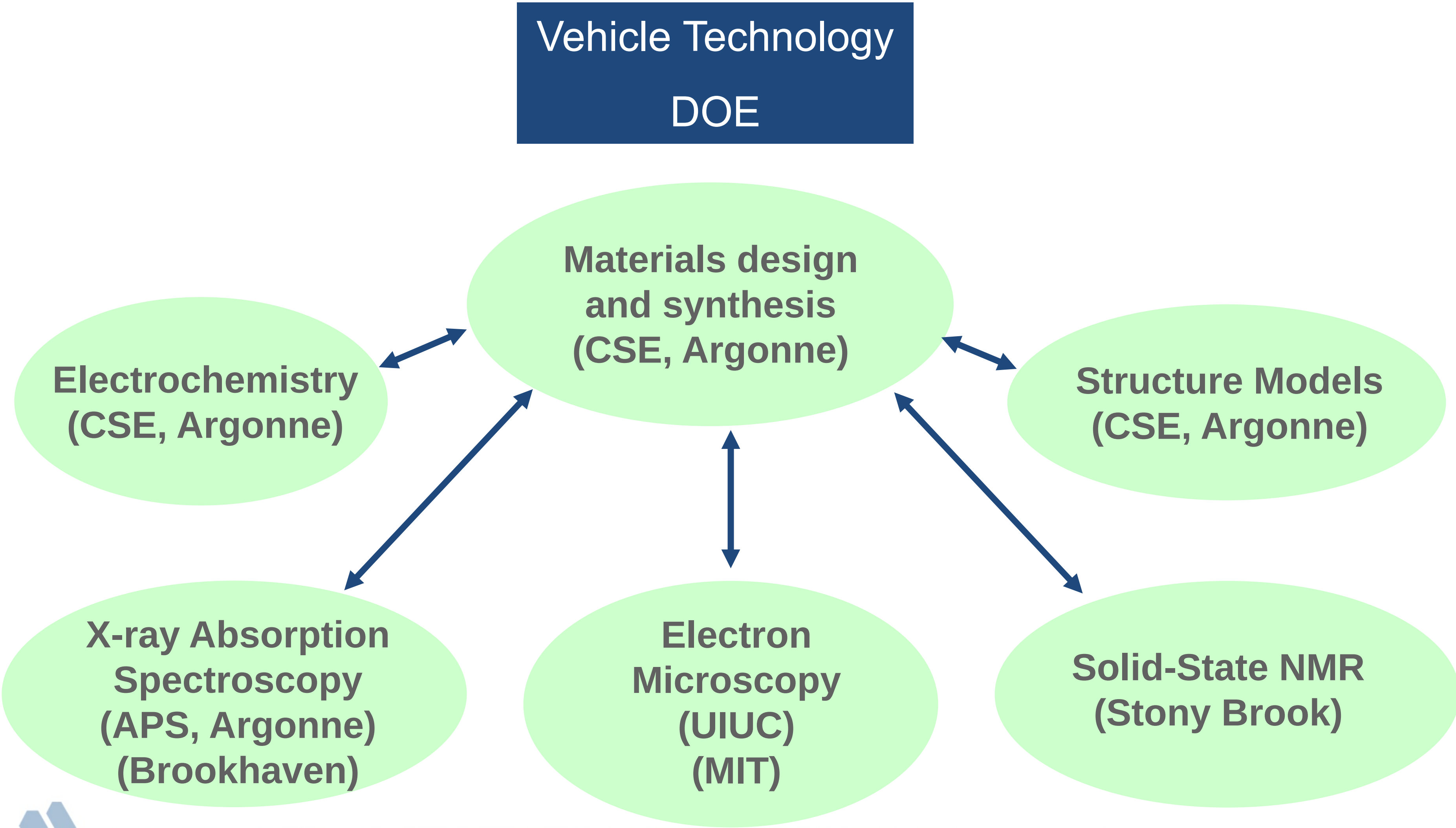
DOE Energy Storage Goals		HEV(2010)	PHEV(2015)	EV(2020)
Characteristics	**Unit**			
Equivalent Electric Range	miles	**N/A**	**10-40**	**200-300**
Discharge Pulse Power	kW	**25-40 for 10 sec**	**38-50**	**80**
Regen Pulse Power (10 seconds)	kW	**20-25**	**25-30**	**40**
Recharge Rate	kW	**N/A**	**1.4-2.8**	**5-10**
Cold Cranking Power @ -30 ºC (2 seconds)	kW	**5-7**	**7**	**N/A**
Available Energy	kWh	**0.3-0.5**	**3.5-11.6**	**30-40**
Calendar Life	Year	**15**	**10+**	**10**
Cycle Life	Cycles	**300k, shallow**	**3,000-5,000, deep discharge**	**750, deep discharge**
Maximum System Weight	kg	**40-60**	**60-120**	**300**
Maximum System Volume	l	**32-45**	**40-80**	**133**
Operating Temperature Range	ºC	**-30 to 52**	**-30 to 52**	**-40 to 85**
Selling Price @ 100k units/year	$	**500-800**	**1,700-3,400**	**4,000**

❖ No commercially available chemistries (cathode, anode, electrolyte, etc.) meet the DOE targets for PHEVs and EVs with 40+ electric range.

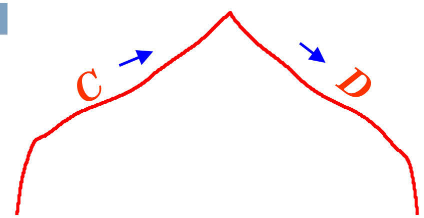
- Key issues: Energy, Life, Safety, and Cost

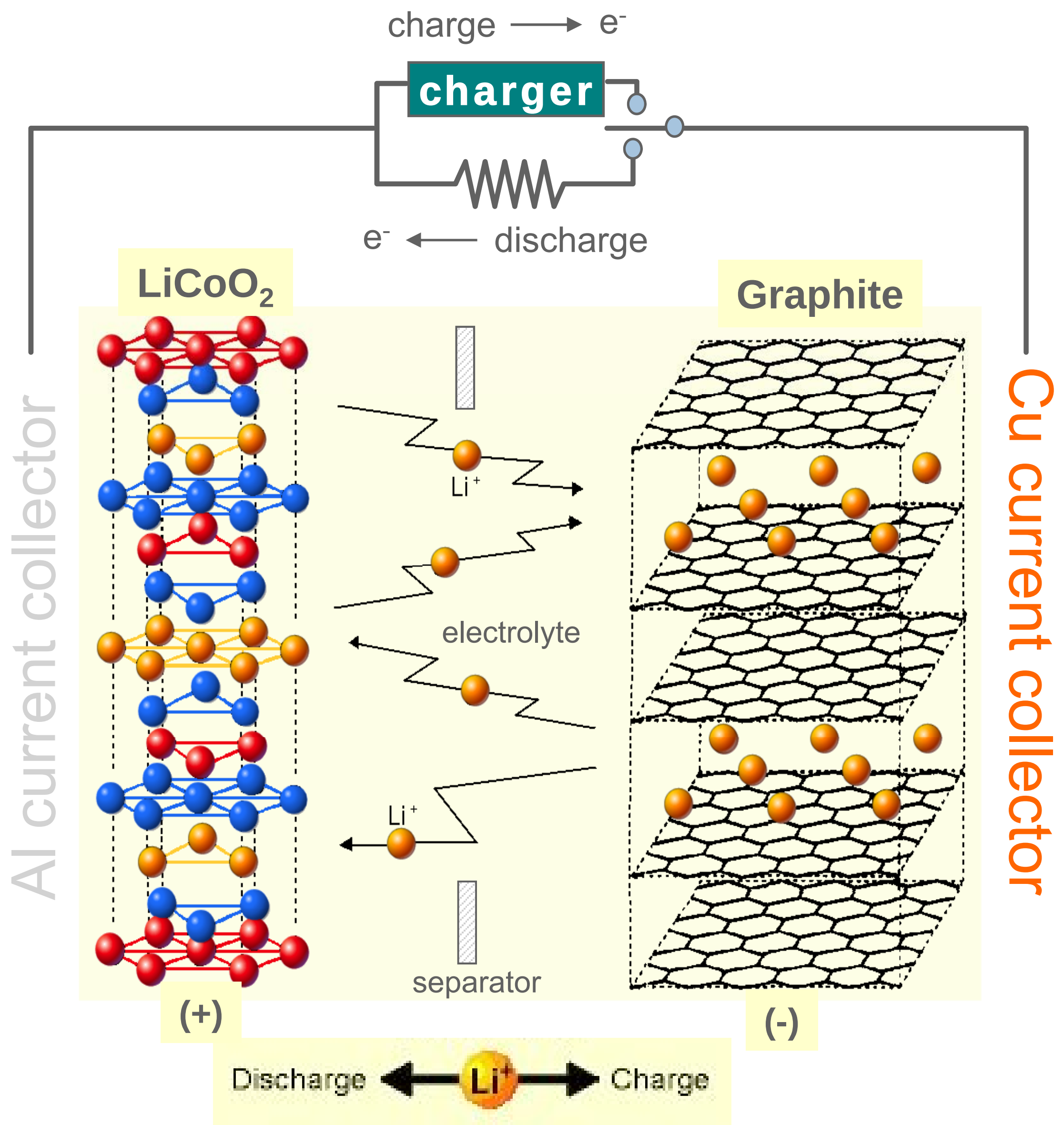
Approach

- Multi-institution team assembled to design, synthesize, characterize, and model oxide structures for next-generation electrode materials



What happens in a Li-ion cell?





Charging

Li → Li^+ + e^-

Requires Energy

Discharging

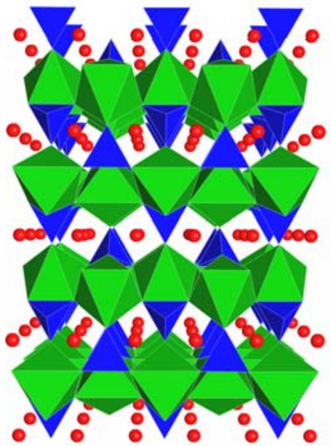
Li^+ + e^- → Li

Supplies Energy

Process reversibility should be ~100% for good cycle life

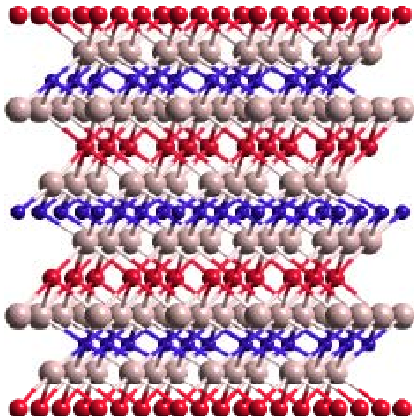
Active material in cathode is the source of lithium ions

$LiMPO_4$
(M=Fe, Ni, Co)



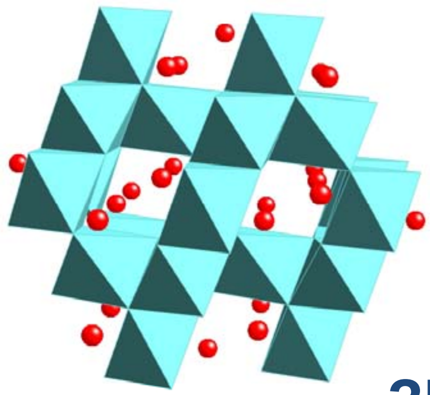
1D

$LiMO_2$
(M=Ni, Co, Mn, Li)



2D

$LiMn_2O_4$



3D

$LiMPO_4$

Pros:

- Excellent safety
- Cost advantage (Fe)

Cons:

- Poor conductivity
- Low theoretical capacity (~170 mAh/g)

$LiMO_2$

Pros:

- High theoretical capacity (~ 280 mAh/g)

Cons:

- Structural destabilization at high SOC
- Highly oxidizing/unstable Ni^{4+} and Co^{4+} poor thermal safety

$LiMn_2O_4$

Pros:

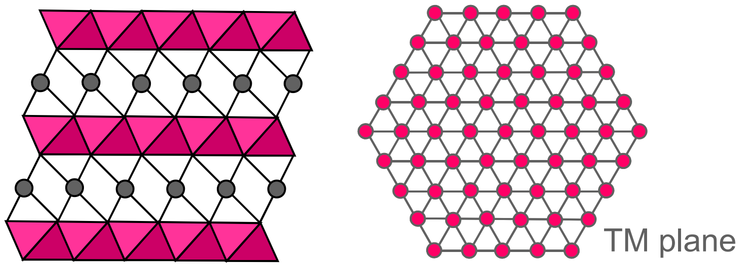
- Fast Li motion through 3D Li channel
- Low cost (Mn-based)

Cons:

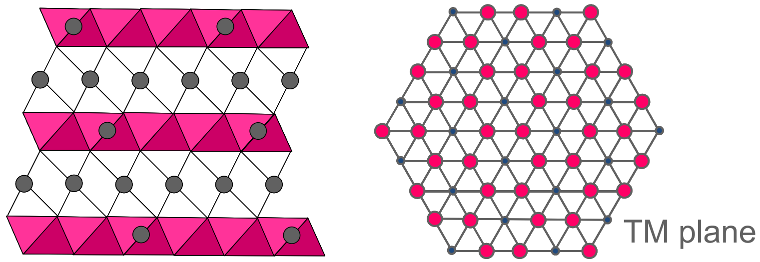
- Low theoretical capacity (~150 mAh/g)
- Capacity fading (Mn dissolution, Jahn-Teller distortion)

Limitations of layered lithium metal oxides

$LiMO_2$ (M=Ni,Co,Mn)



$Li(Li_{1/3}Mn_{2/3})O_2$ ($\equiv Li_2MnO_3$)



➢ *For last two decades, layered $LiMO_2$ (mostly $LiCoO_2$) has been the positive electrode chemistry of choice for the LIBs for portable electronics.*

➢ *Limitations*

- High cost of Co and Ni
- Low practical conductivity (~150 mAh/g vs. ~280 theoretical capacity of $LiCoO_2$) due to the structural instability at low Li content (Li/M<0.5)
- Conversion to spinel during cycling ($LiMnO_2$)
- Highly unstable and oxidizing Ni^{4+} and Co^{4+} at charged state: thermal safety issues

Not a good electrode material for high energy Li-ion batteries with intrinsic thermal safety!

➢ *Similar structure to $LiMO_2$*

- One-third of M is replaced with Li
- Strong ordering between Li^+ and Mn^{4+}

➢ *Electrochemistry*

- at <4.4 V vs. Li^+/Li, Li_2MnO_3 is electrochemically inactive
- At >4.4 V vs. Li^+/Li, lithium can be extracted together with oxygen:

$$Li_2Mn^{4+}O_3 \rightarrow Li_2O + Mn^{4+}O_2 \text{ (460 mAh/g)}$$

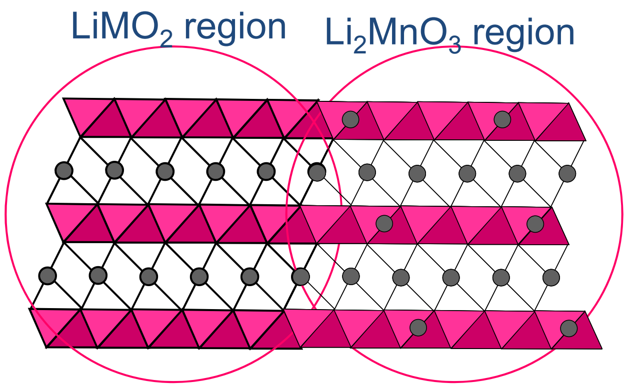
- However, the activated electrode tends to convert to spinel with cycling (same issue as $LiMnO_2$)

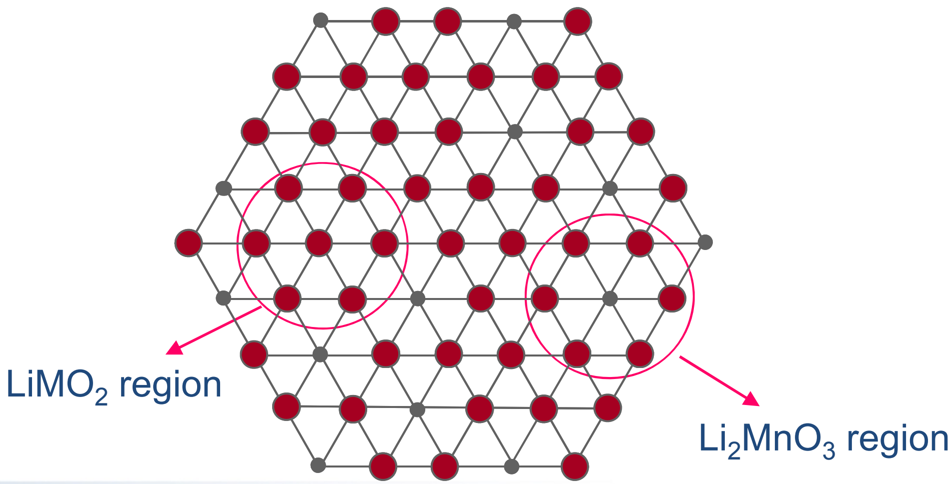
Not a good electrode material for high energy Li-ion batteries with longevity!

Nano-composite among Li_2MnO_3, $LiMO_2$, and LiM'_2O_4

- A unique approach of integrating lithium metal oxides with structural compatibility in nano-composite structures:
  (1) 'layered-layered' electrodes with layered Li_2MnO_3 and $LiMO_2$ components
  (2) 'layered-layered-spinel' electrodes comprised of layered Li_2MnO_3, layered $LiMO_2$ and spinel LiM'_2O_4 components.
- Motivation
  - Enhancing structural stability: integration of Li_2MnO_3 as a structural stabilizing agent in $LiMO_2$ matrix to prevent structure collapse of the layered structure at low Li content
  - Increasing capacity: activation of Li_2MnO_3 at high voltages

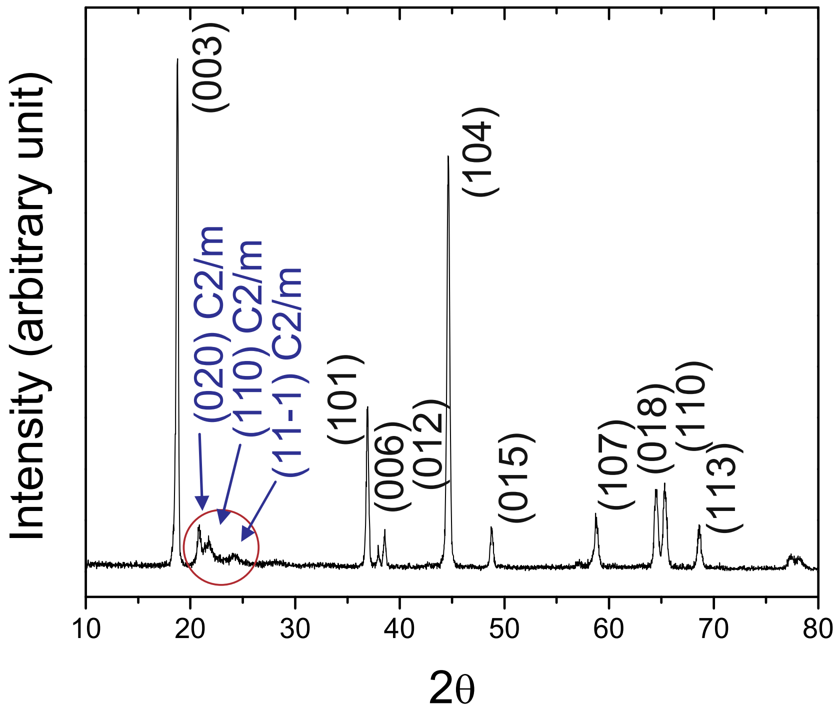
An example of layered-layered nano-composite structure



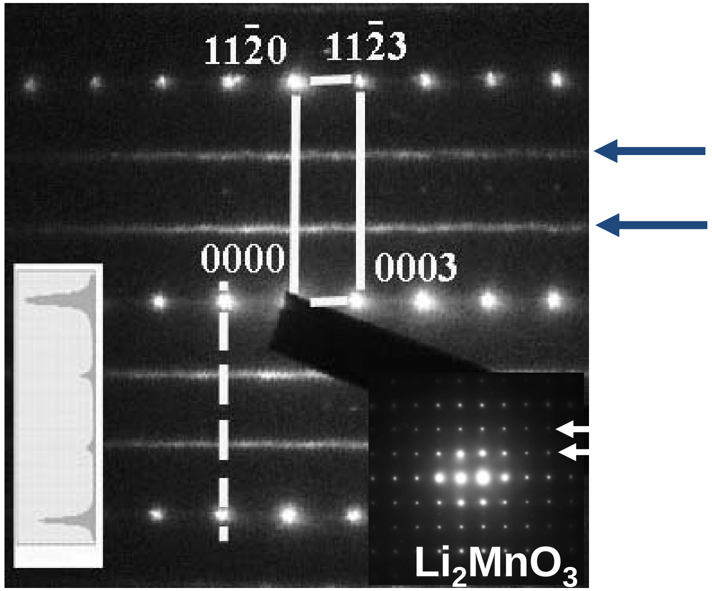


Structural compatibility of Li_2MnO_3 and $LiMO_2$: $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$

XRD pattern



Electron diffraction

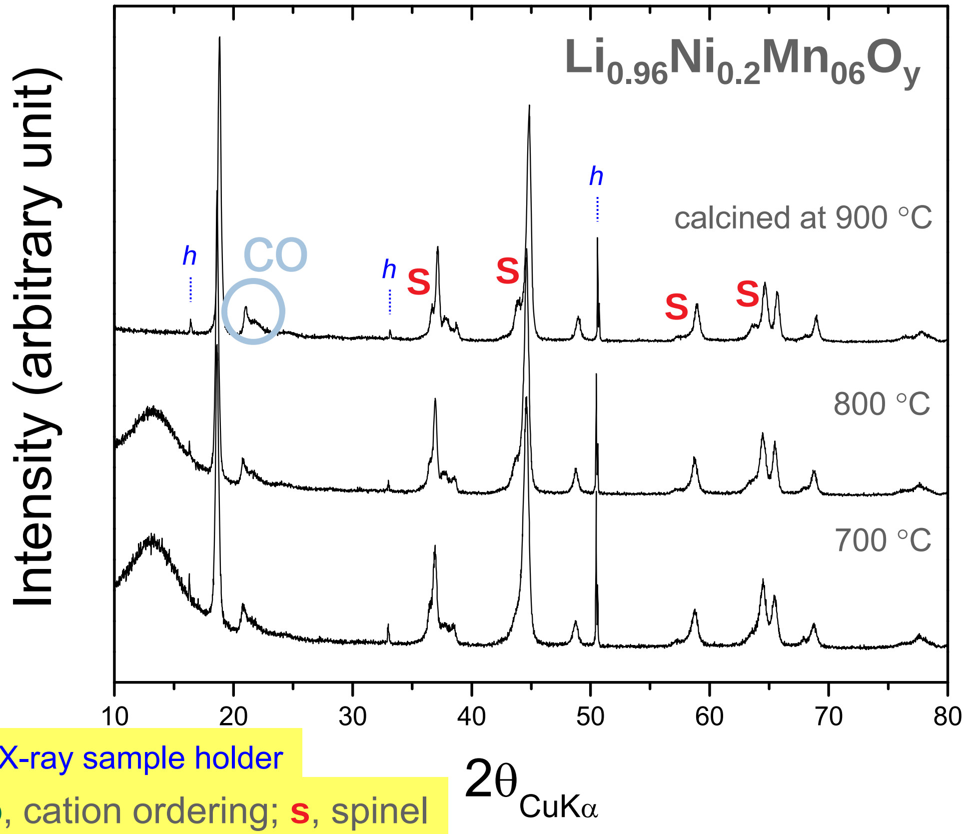


➢Mostly $LiMO_2$-like (rhombohedral, R-3m) feature with Li_2MnO_3-like (monoclinic, C2/m) characters (cation ordering peaks and diffuse streaks)

➢$Li_{1.2}Ni_{0.2}Mn_{0.6}O_2 \equiv$ **$0.5Li_2MnO_3 \bullet 0.5LiNi_{0.5}Mn_{0.5}O_2$**

Structural compatibility of Li_2MnO_3, $LiMO_2$, and LiM'_2O_4: $Li_{0.96}Ni_{0.2}Mn_{0.6}O_y$ (y~1.88)

X-ray diffraction patterns



h: X-ray sample holder

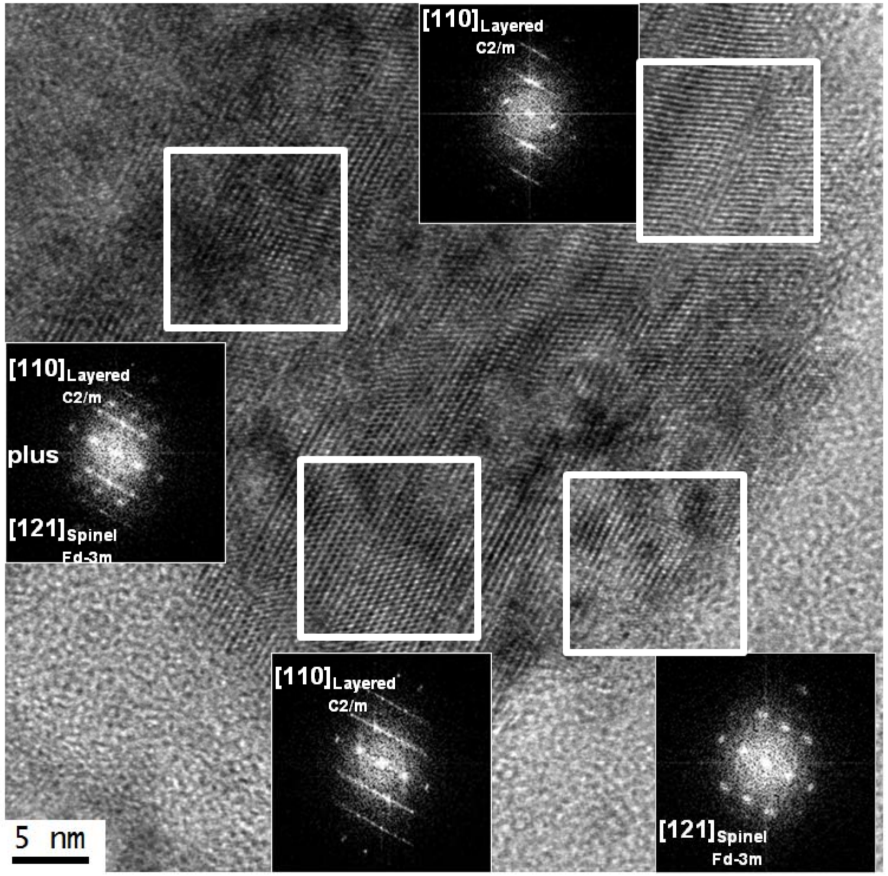
co, cation ordering; **s**, spinel

$LiMO_2$ (layered) + Li_2MnO_3 (layered with cation ordering) + LiM'_2O_4 (spinel)

- Three-component integrated structure
- $Li_{0.96}Ni_{0.2}Mn_{0.6}O_y \equiv$ **$0.3LiNi_{0.5}Mn_{1.5}O_4 \bullet 0.7Li_2MnO_3 \bullet 0.7LiMO_2$ ($M=Ni_{0.5}Mn_{0.5}$)**

Nano-composite feature of $Li_{0.96}Ni_{0.2}Mn_{0.6}O_y$: $0.3LiNi_{0.5}Mn_{1.5}O_4 \bullet 0.7Li_2MnO_3 \bullet 0.7LiMO_2$ (M=$Ni_{0.5}Mn_{0.5}$)

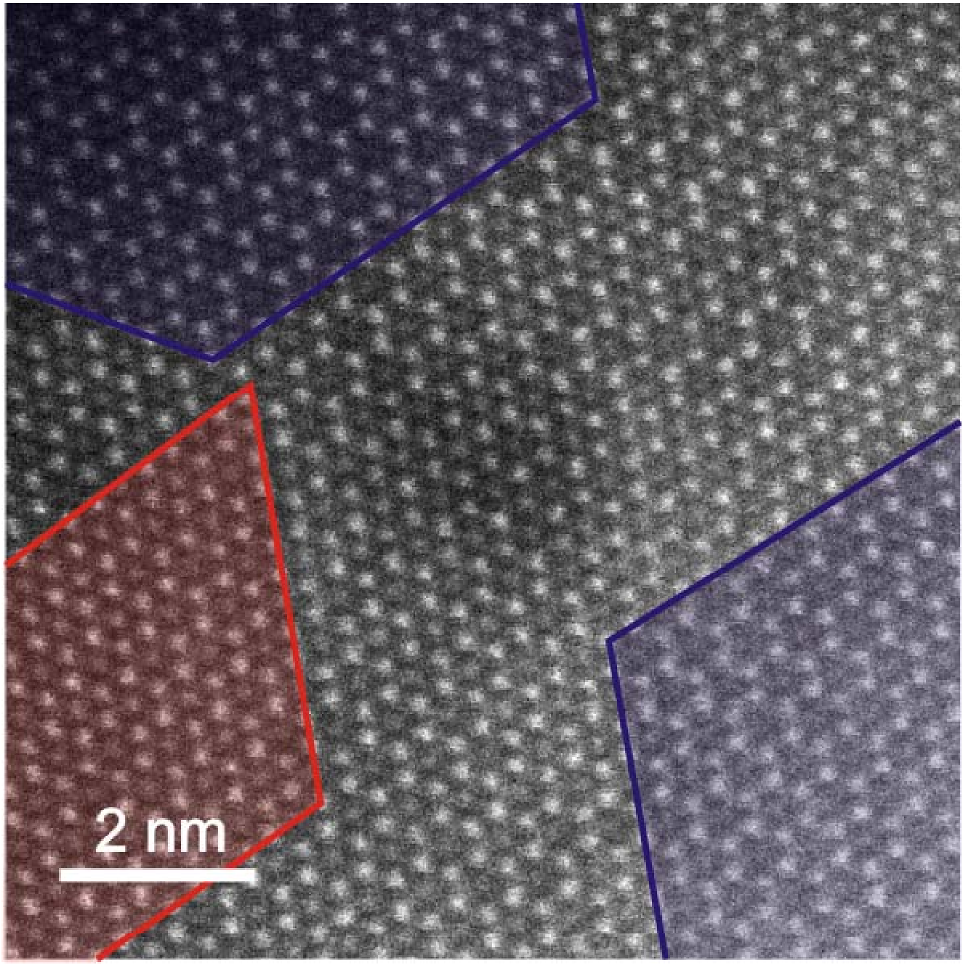
HR TEM image



This HR TEM image demonstrates the structural integration of spinel (Fd-3m) and layered (C2/m).

Nano-composite feature of $Li_{1.2}Co_{0.4}Mn_{0.4}O_2$: $0.5Li_2MnO_3 \cdot 0.5LiMO_2$ (M=Co)

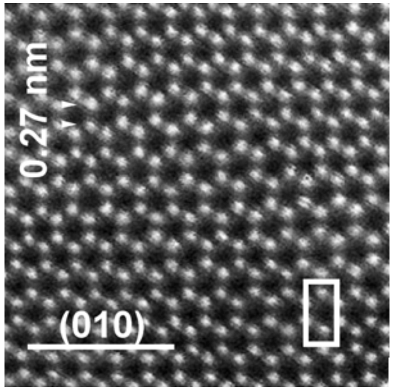
Z contrast STEM image

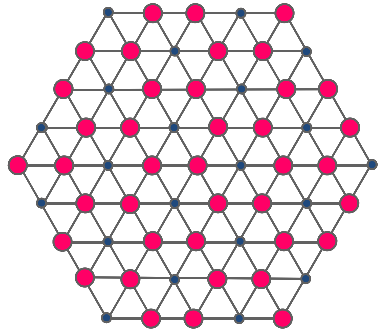


View of transition metal planes along $[001]_M$

TM columns: bright-spots in image
Li columns: dark.

Honeycomb regions (hollow core = Li column) are Li_2MnO_3-like. Hexagonal regions (filled core = TM column) are $LiCoO_2$-like. No sharp boundaries between honeycomb and hexagonal regions.

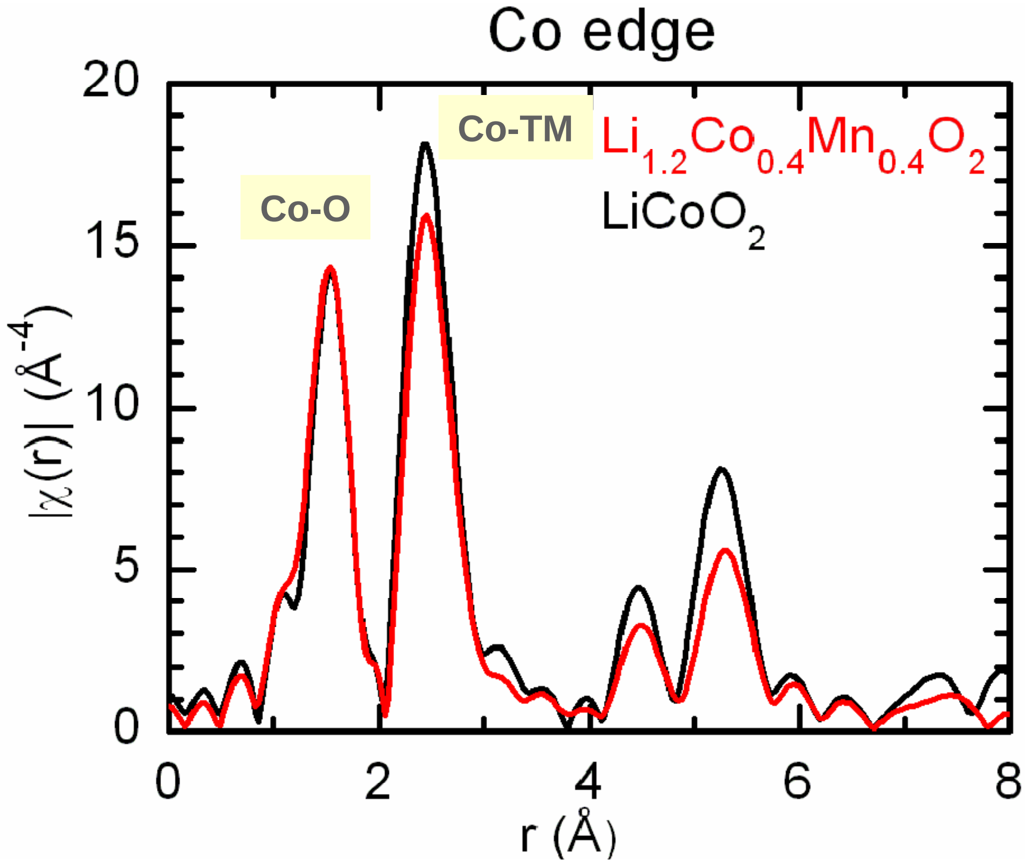




Li_2MnO_3

X-ray absorption spectroscopy of $0.5Li_2MnO_3 \cdot 0.5LiCoO_2$

Co EXAFS



$0.5Li_2MnO_3 \cdot 0.5LiCoO_2$

Co-O bond distance ~ 1.91 Å (same as in $LiCoO_2$)

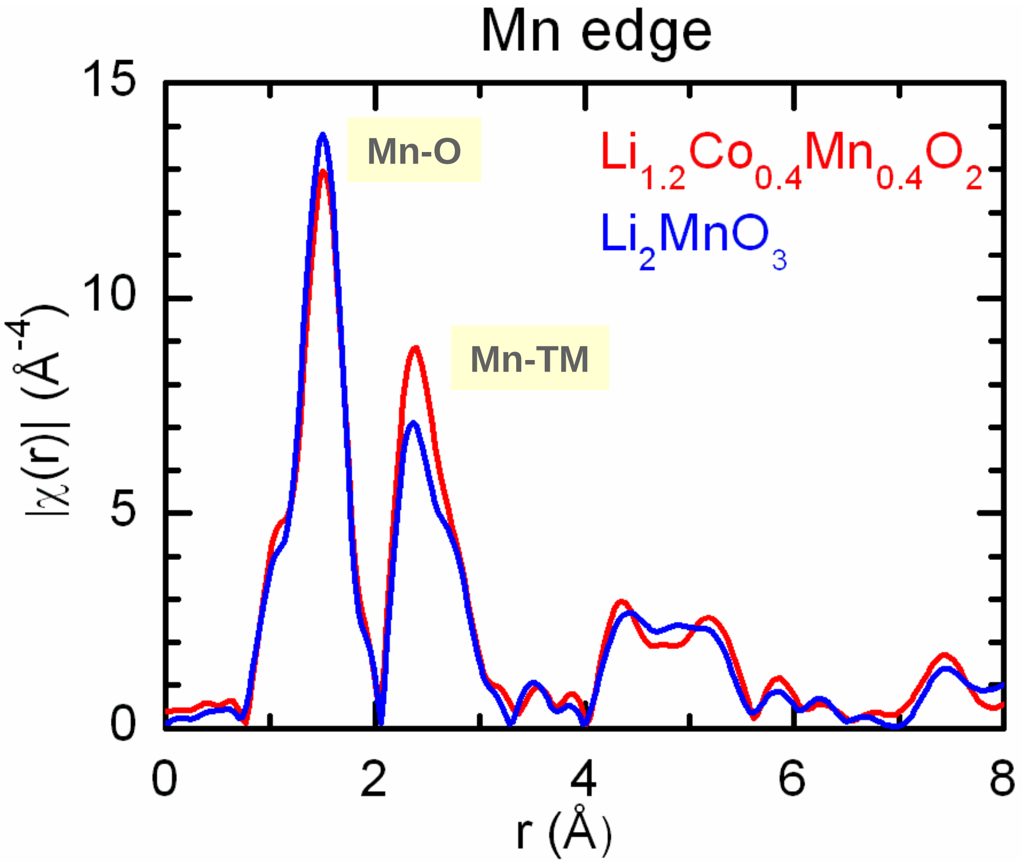
Co-TM data coordination is 5.4 +/- 0.5 (6 in $LiCoO_2$)

Exact phase matching of peaks in 4-6 Å range *(data not shown)*

Co environment in $0.5Li_2MnO_3 \cdot 0.5LiCoO_2$ appears very similar to $LiCoO_2$ environment up to 7 Å.

X-ray absorption spectroscopy of $0.5Li_2MnO_3 \bullet 0.5LiCoO_2$

Mn EXAFS



$0.5Li_2MnO_3 \bullet 0.5LiCoO_2$

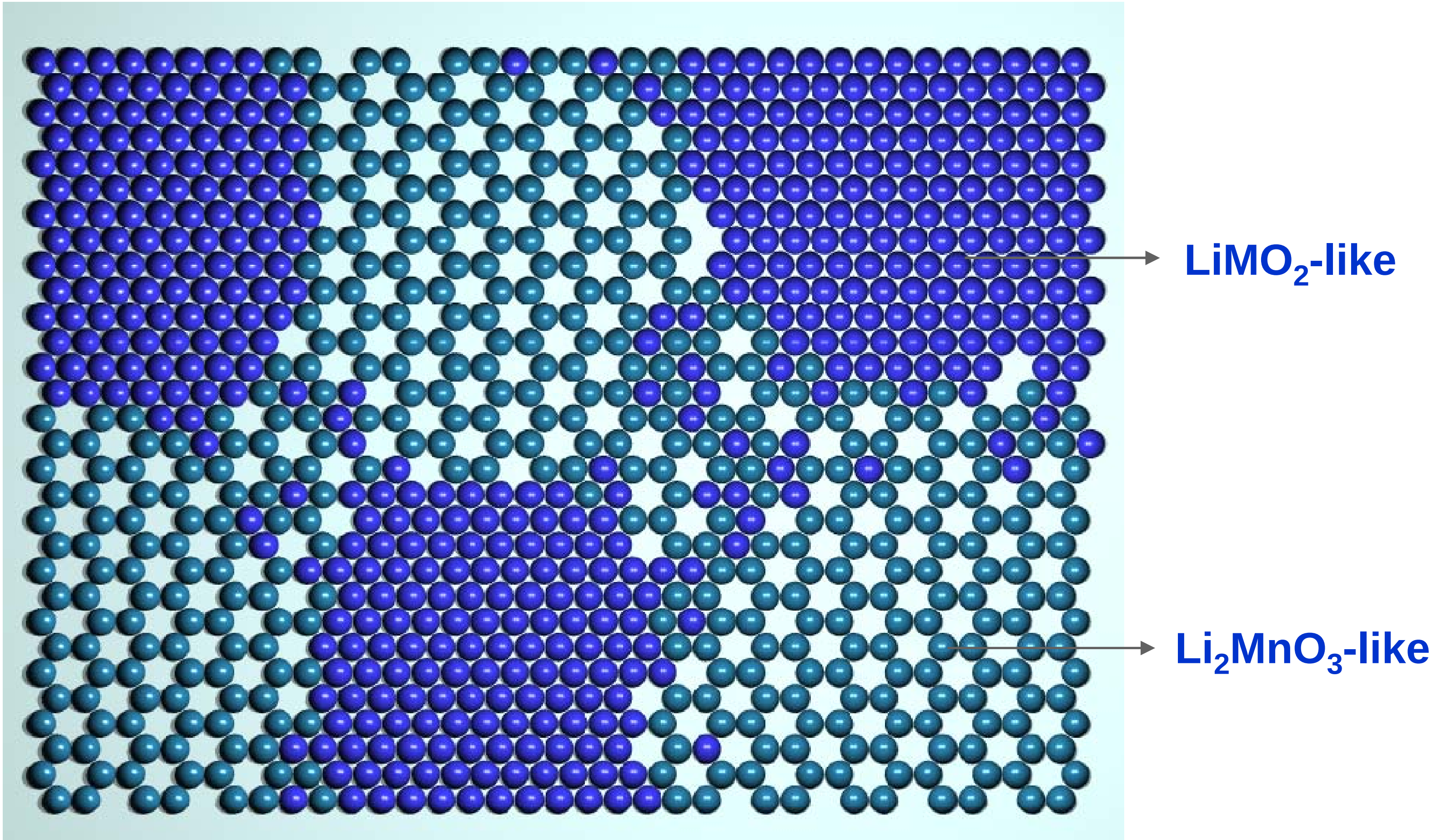
Mn-O bond distance ~ 1.89 Å (same as in Li_2MnO_3)

Mn-TM data coordination is 4.2 +/- 0.5 (3 in Li_2MnO_3)

Exact phase matching of peaks in 4-6 Å range *(data not shown)*

Mn environment in $0.5Li_2MnO_3 \bullet 0.5LiCoO_2$ appears similar to Li_2MnO_3 environment up to 7 Å.

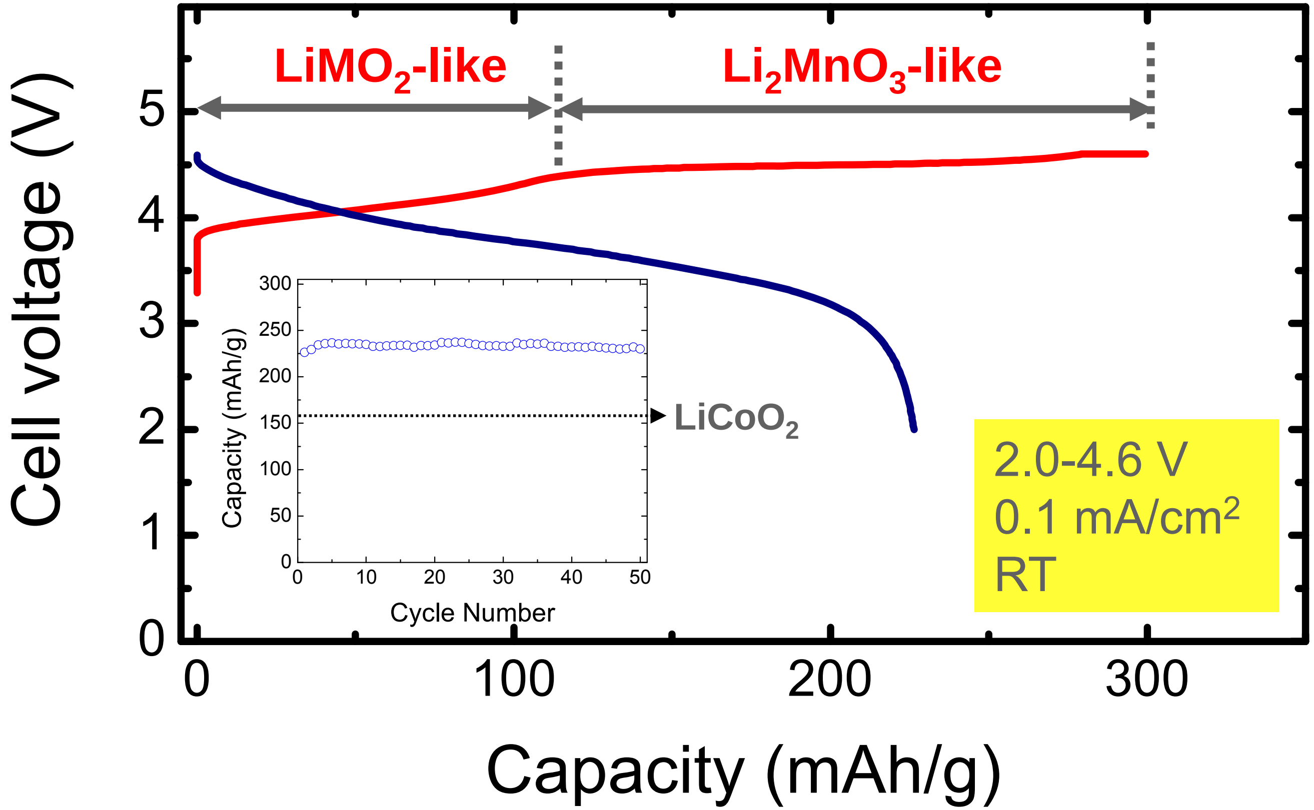
Model for atomic arrangement in TM plane of $0.5Li_2MnO_3 \bullet 0.5LiMO_2$



An intimate mixture of $LiMO_2$-like and Li_2MnO_3-like areas (~1-3 nm size) are present in $0.5Li_2MnO_3 \bullet 0.5LiMO_2$

Electrochemistry of two-component system

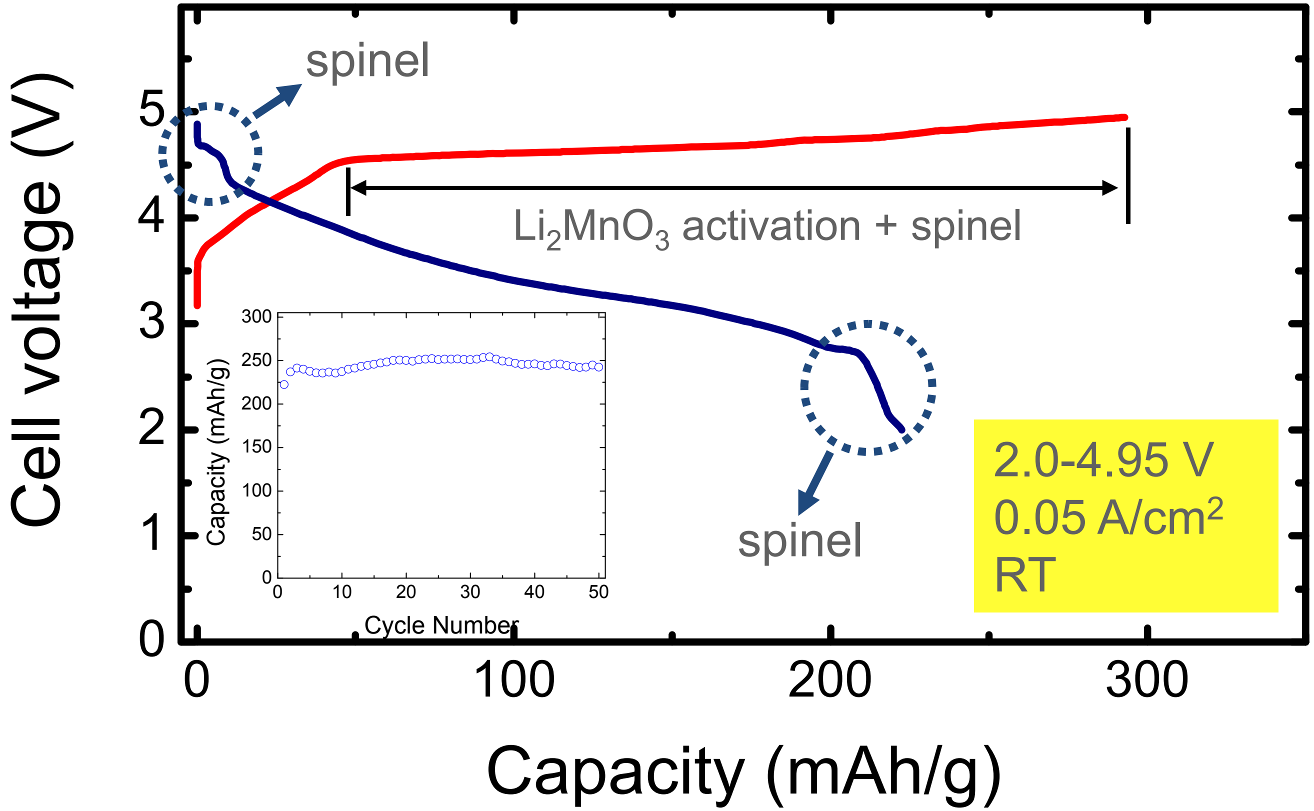
$Li_{1.2}Ni_{0.18}Co_{0.10}Mn_{0.52}O_2$: *First cycle profile of a lithium cell*



- Two step behavior during the first charge:
  - $LiMO_2$-like region: $LiMO_2 \rightarrow Li^+ + MO_2 + e^-$
  - Li_2MnO_3-like region: $Li_2MnO_3 \rightarrow 2Li^+ + MnO_2 + 1/2O_2 + 2e^-$ (O_2 evolution confirmed by in situ DEMS)
- Very high capacity during the subsequent discharge and excellent capacity retention

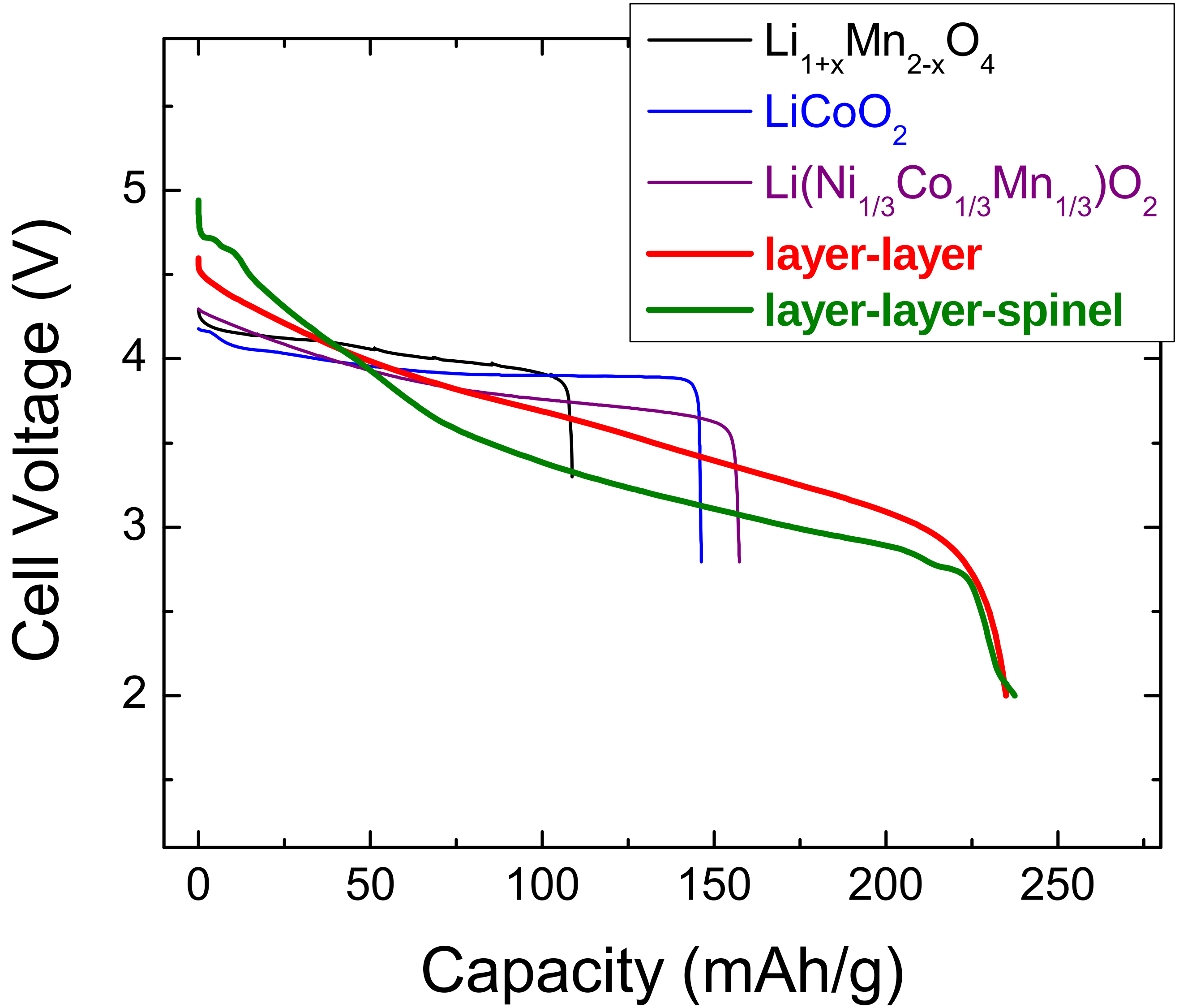
Electrochemistry of three-component system

$Li_{0.96}Ni_{0.2}Mn_{0.6}O_y$: *First cycle profile of a lithium cell*

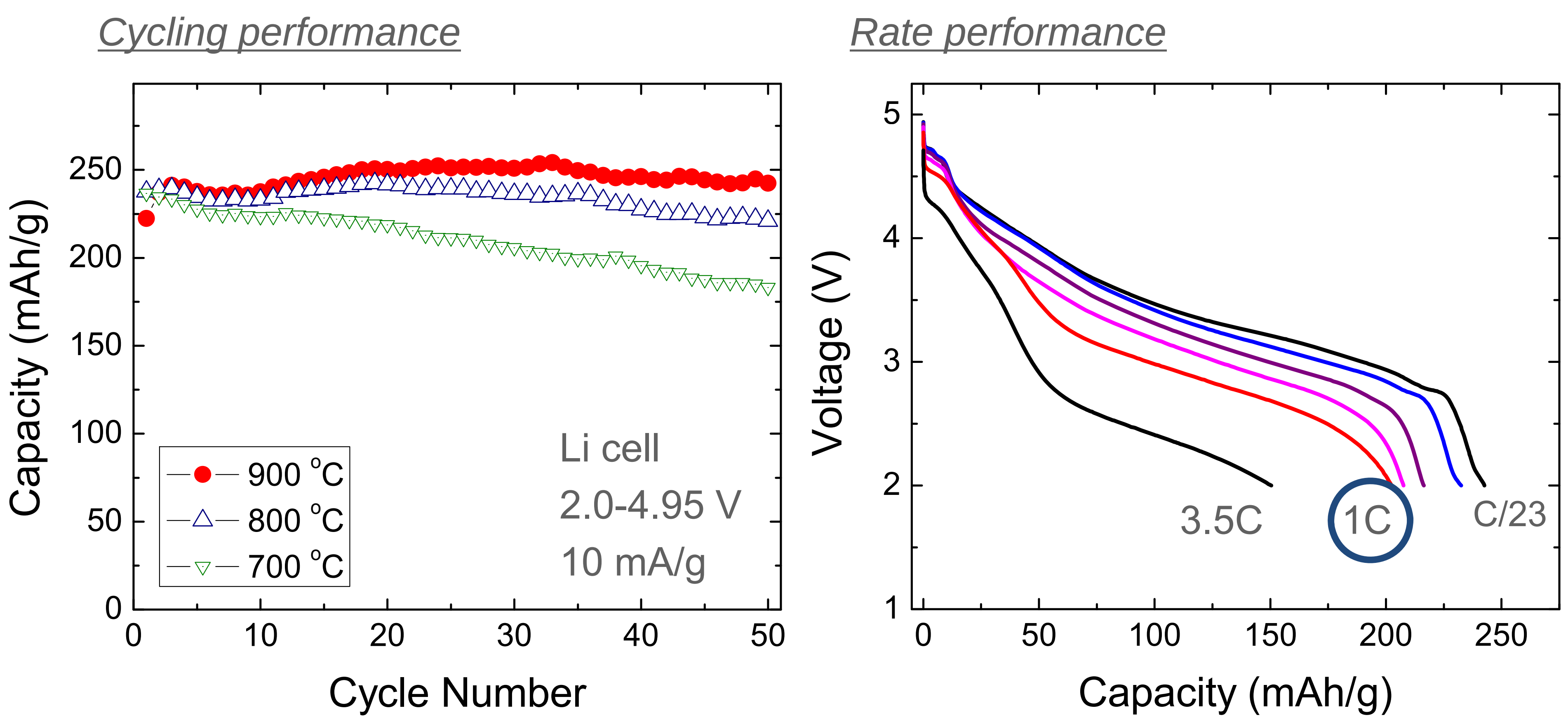


- Three distinctive regions:
  $LiMO_2$-like region, Li_2MnO_3-like region (activation), and spinel signatures
- Very high capacity during the subsequent discharge and excellent capacity retention

Superior electrochemical property of the nano-composite electrode material to other materials



Capacity Retention and Rate Capability of $Li_{1.2}Ni_{0.25}Mn_{0.75}O_y$



- Beneficial impact of the spinel component in the structure
  - Excellent cycling performance (800, 900 °C samples) in spite of the very high cut-off voltage.
  - Good rate capability (~200 mAh/g at 1C rate).

SUMMARY

- A novel concept of integrating lithium metal oxides with different structures (but compatible) in nano-scale has been adopted to design and develop electrode materials for advanced high-energy lithium-ion batteries.
  - Two component system
  - Three-component system
- Through advanced analytic techniques, the atomic arrangement features of the nano-composite materials have been demonstrated.
- The nano-composite material exhibited outstanding electrochemical performance.
- Possibility of using these nano-composite electrode materials in PHEV batteries is under investigation.
- The Argonne's nano-composite cathode materials have recently been licensed to major chemical companies and battery companies.

Acknowledgement

Argonne National Laboratory

- CSE Division: M. M. Thackeary, C. S. Johnson, D. P. Abraham, J. Bareno, G. Henriksen
- APS: M. Balasubramanian – XAS

UIUC

- C. H. Lei, I. Petrov – TEM
- C. Carlton, Y. Shao-Horn – TEM

Department of Energy

- Office of Basic Energy Sciences – ‘fundamental research’
- Office of FreedomCar and Vehicle Technologies – ‘exploratory (BATT) and applied (ABRT) R&D’