Advanced *in situ* Diagnostic Techniques for Battery Materials

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ES059

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BROOKHAVEN NATIONAL LABORATORY

Overview

Timeline

- ▣ Start: 10/01/2013
- ▣ Finish: 09/30/2016

Barriers addressed

- To reduce the production cost of a PHEV battery
- Li-ion and Li-metal batteries with long calendar and cycle life
- Li-ion and Li-metal batteries with superior abuse tolerance

Budget

- ▣ Funding received in FY14

  DOE: $415k
- ▣ Funding received in FY15

  DOE: $415k

Collaborators

- University of Wisconsin at Milwaukee
- Drexel University
- Massachusetts Institute of Technology (MIT)
- Lawrence Berkeley National Laboratory (LBNL)
- Pak Ridge National Lab. (ORNL)
- Argonne National Lab. (ANL)
- Pacific Northwest National Lab. (PNNL)
- Johnson Control Inc.

- Beijing Institute of Physics
- Hydro-Québec (IREQ)

Relevance and Project Objectives

✓ ***Diagnostics study of thermal abuse tolerance (to improve the safety characteristics of electrode materials).***

- ➥ to establish and investigate the structural origin of thermal instability of various cathode materials, especially the high voltage $LiNi_{0.5}Mn_{1.5}O_4$ materials
- ➥ to search new approaches on how to improve the thermal stability of cathode materials including doping and surface modification techniques.
- ➥ to provide valuable information about how to design thermally stable cathode materials for HEV and PHEV applications.
- ➥ to develop new *in situ* diagnostic techniques with surface and bulk sensitivity for studying the thermal stability of various cathode materials.

✓ ***Diagnostics study aimed to improve the calendar and cycle life of batteries.***

- ➥ to develop in situ diagnostic techniques with surface and bulk sensitivity to improve the calendar and cycle life of batteries by studying the mechanism of capacity, voltage, and power fading of Li-ion battery.

✓ ***Diagnostics study of electrode materials with lower cost potential.***

Milestones

Month/Year	Milestones
Dec/14	Complete the thermal stability studies of a series of blended $LiMn_2O_4$ (LMO) - $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) cathode materials with different weight ratios using in situ time-resolved x-ray diffraction (XRD) and mass spectroscopy techniques in the temperature range of 25° C to 580° C ↪ *Completed.*
Mar/15	Complete the In situ XRD studies of the structural evolution of $Li_{2-x}MoO_3$ ($0 \leq x \leq 2$) high energy density cathode material during charge-discharge cycling between 2.0 and 4.8 V. ↪ *Completed.*
Jun/15	Complete the x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) studies at Mo K-edge of Li_2MoO_3 at different charge-discharge states. ↪*On schedule.*
Sep/15	Complete the preliminary studies of elemental distribution of Fe substituted high voltage spinel cathode materials using transmission x-ray microscopy (TXM). ↪ *On schedule.*

Approaches

- A combination of time resolved X-ray diffraction (TR-XRD) and mass spectroscopy (MS), together with *in situ* soft and hard X-ray absorption (XAS) during heating and transmission electron microscopy (TEM) to study the thermal stability of the electrode materials.

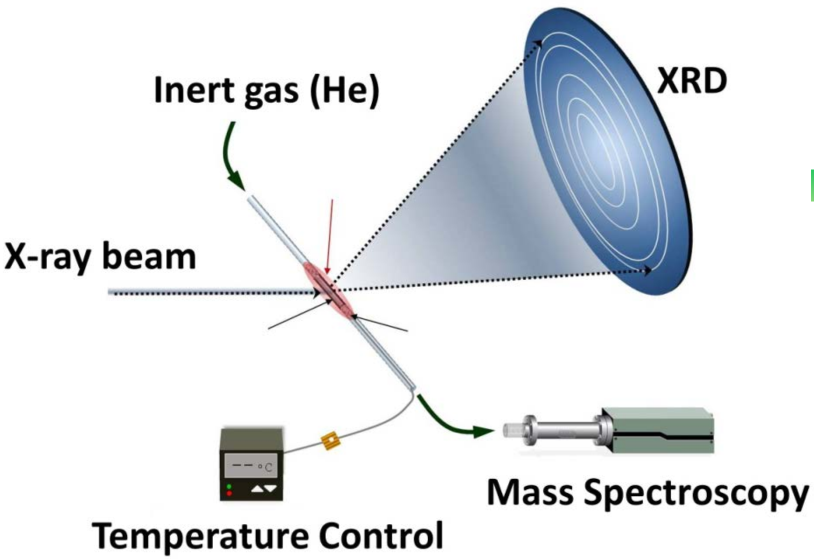
- Using *in situ* XRD and XAS, as well as TEM to study a model cathode material Li_2MoO_3 on the lattice breathing of layer structured materials during charge-discharge cycling, aiming to improve the cycle life of Li-ion batteries

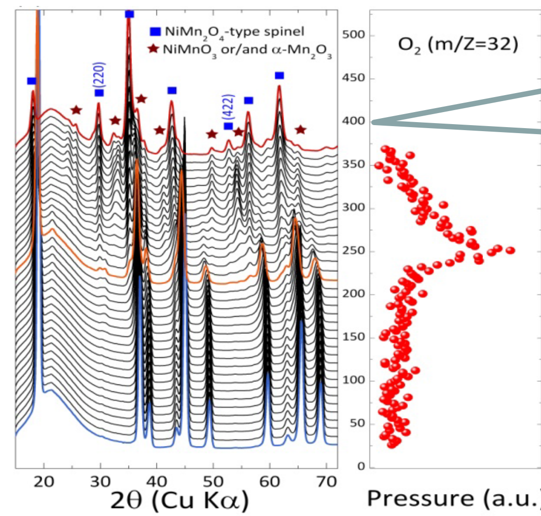
- Using quick x-ray absorption spectroscopy technique to study the kinetic properties of $Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$ high energy density cathode materials during constant voltage charge for high rate capability of Li-ion batteries.

- Extended collaboration with other US and international academic institutions and US industrial partners.

In Situ Techniques to Address the Mechanism

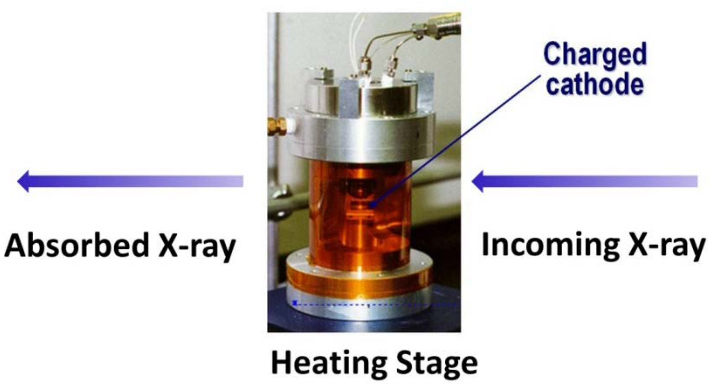
In situ XRD

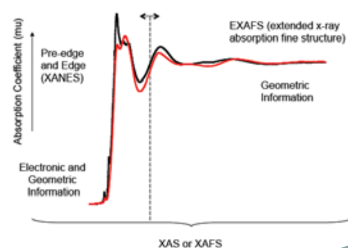


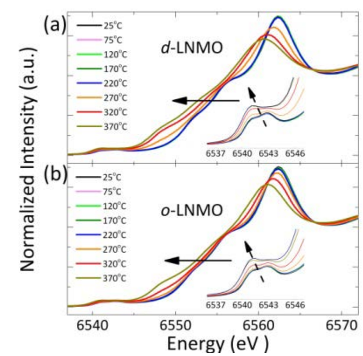


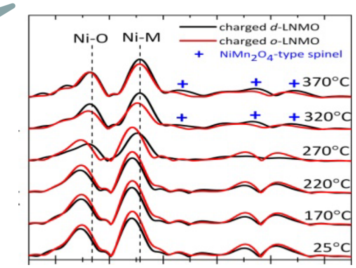
Crystal Structure and Gas Evolution

In situ XAS









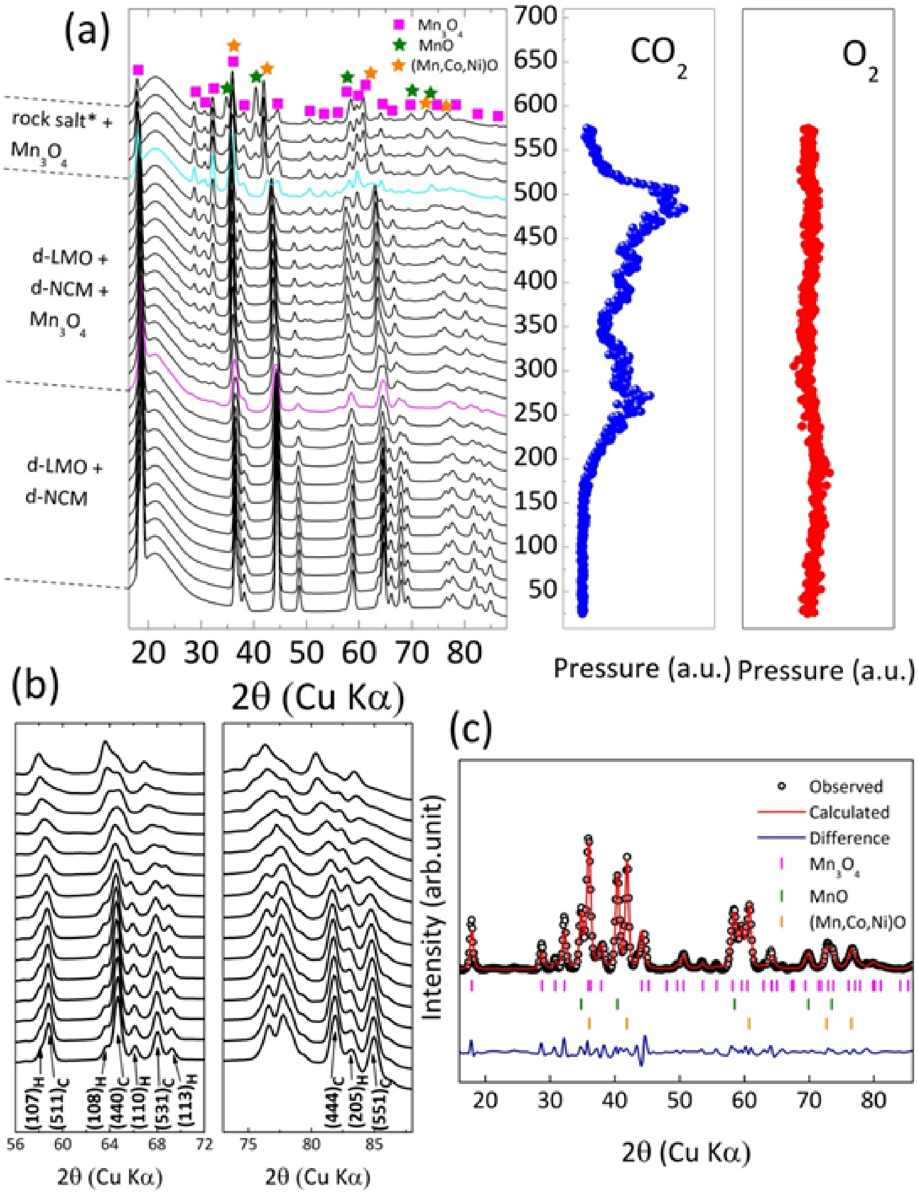
Electronic Structure and Local Environment

S.Bak et al, Chem. Mater. 2013
K.Nam et al, Adv. Funct. Mater. 2013

Technical Accomplishments

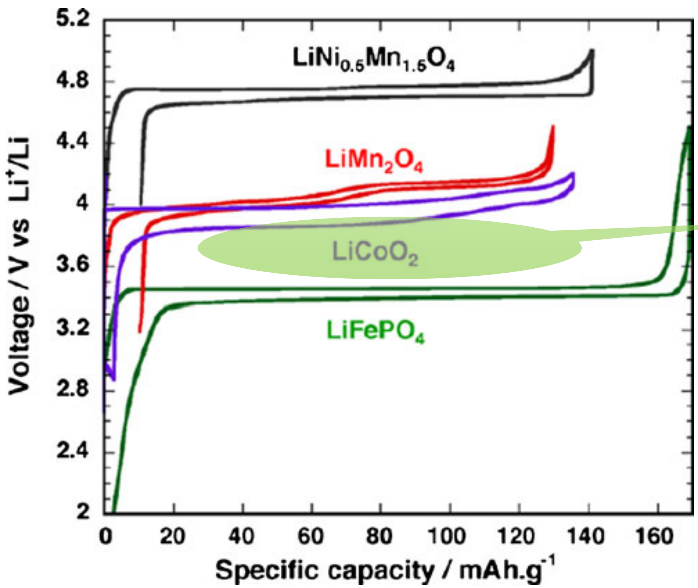
- By collaborating with Prof. Minhua Shao at Hong Kong University of Sciences and Technologies, carried out the thermal stability studies of a series of blended $LiMn_2O_4$ (LMO) -$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) cathode materials with different weight ratios using in situ time-resolved x-ray diffraction (XRD) and mass spectroscopy techniques in the temperature range of 25°C to 580°C .
- By collaborating with Prof. Zhaoxiang Wang at Institute of Physics, Chinese Academy of Sciences, through a systematic study of lithium molybdenum trioxide (Li_2MoO_3) using synchrotron based XRD and XAS, as well as STEM, a new “unit-cell-breathing” mechanism during charge-discharge was discovered. The cation mixing caused by migration of Mo ions at higher oxidation state provides the benefits of reducing the c expansion range in early stage of charging and suppressing the structure collapse at high voltage charge. These results open a new strategy for designing and engineering layered cathode materials for high-energy-density lithium-ion batteries.
- By designed Fe substitution, the thermal stability optimized high voltage spinel $LiNi_{1/3}Mn_{4/3}Fe_{1/3}O_4$ was synthesized and characterized, which is thermally stable at temperature as high as 500° C. Elemental distribution of Fe substituted high voltage spinel cathode materials was studied using new technique of transmission x-ray microscopy (TXM).

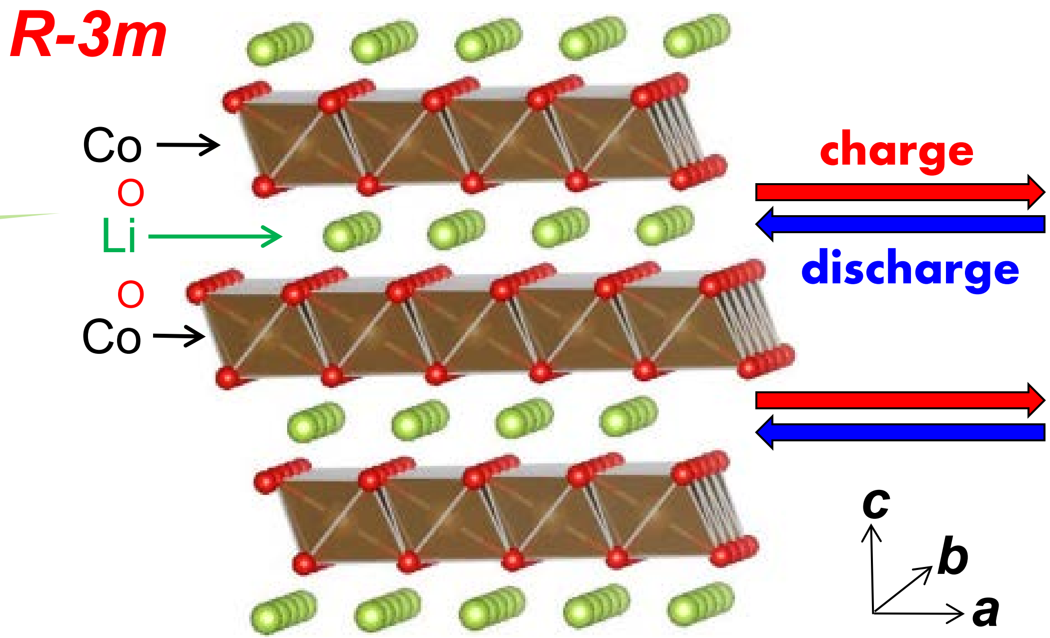
In situ XRD-MS data of electrochemically delithiated LMO and NCM mixture with weight ratio of 3:1



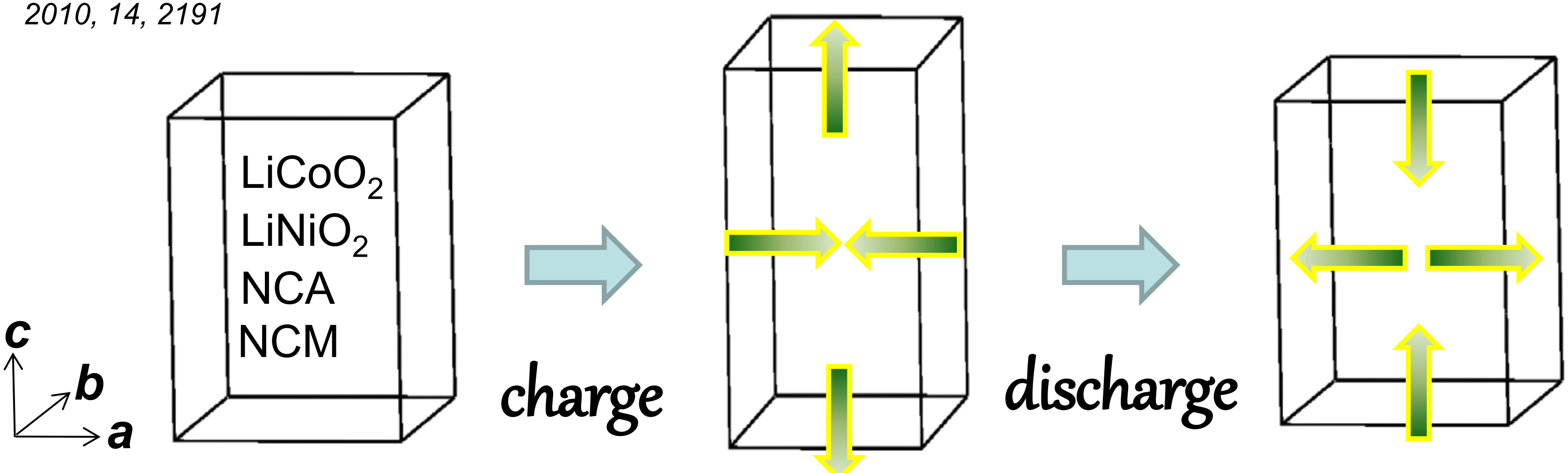
(a) *In situ* XRD-MS data of electrochemically delithiated LMO and NCM mixture with weight ratio of 3:1, and (b) zoomed in XRD patterns with $(hkl)_H$ and $(hkl)_C$ indexed for hexagonal NCM and cubic LMO respectively; patterns are only shown up to 300° C for clarity. (c) LeBail fitting of the XRD pattern at 580 ° C. *rock salt phases include MnO and (Mn,Co,Ni)O; their forming temperatures are close to each other.

Background of "Unit Cell Breathing" of layer-structured cathode materials

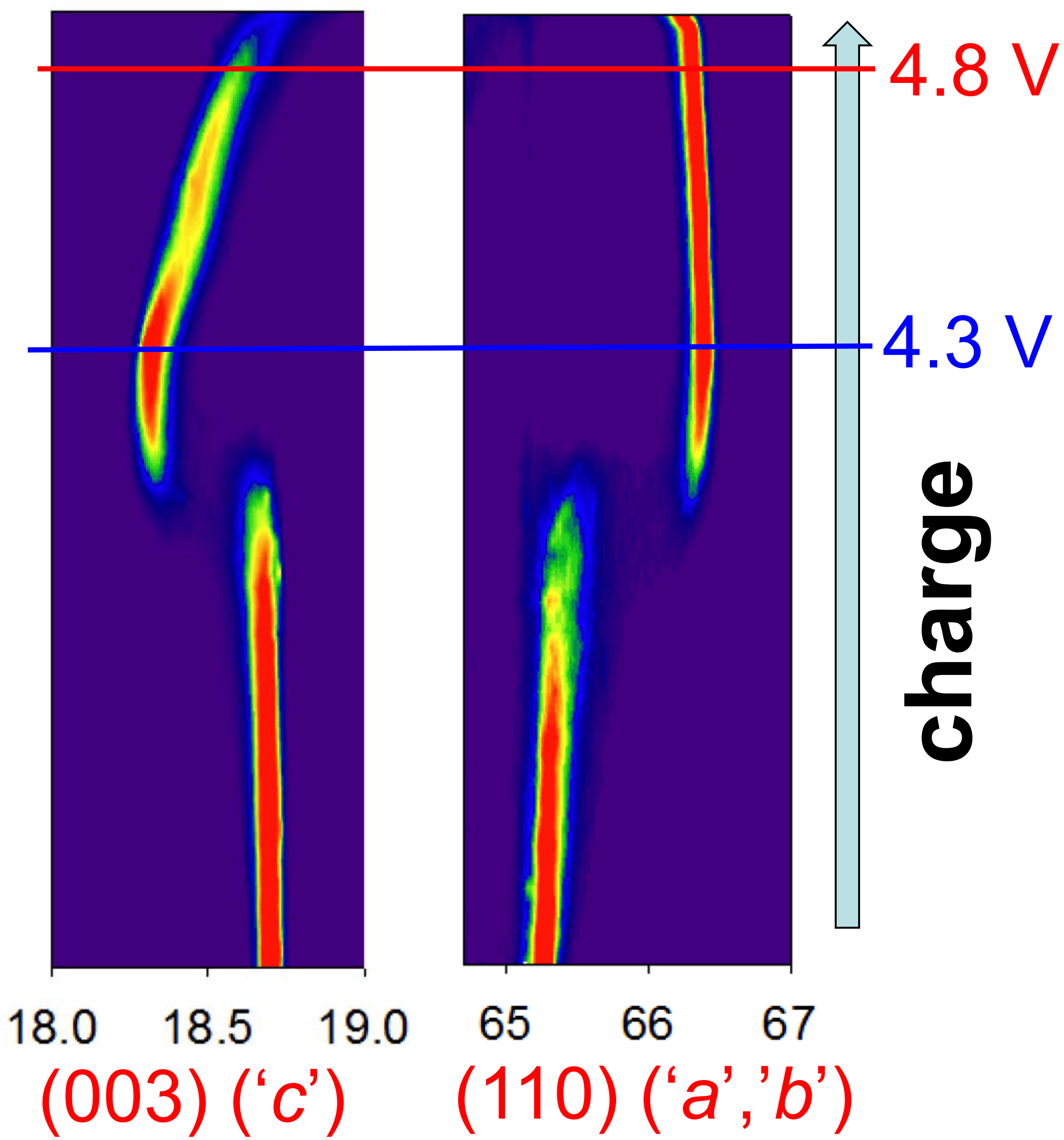




Q. D. Liu et al., J. Solid State Electrochem. 2010, 14, 2191



“Unit Cell Breathing” of layered $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ during charge



‘a’ and ’b’ ↑

‘c’ ↓

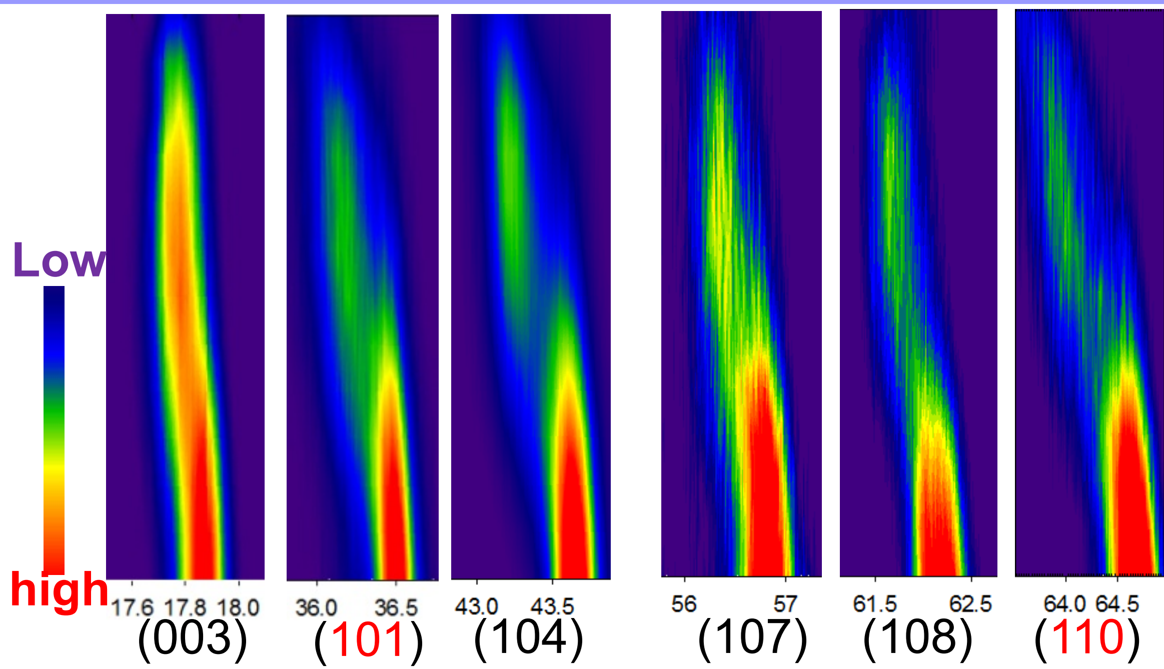
Irreversible !

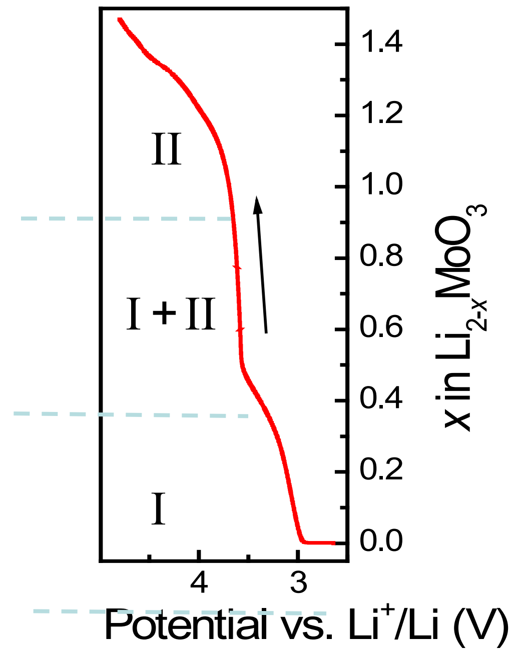
‘a’ and ’b’ ↓

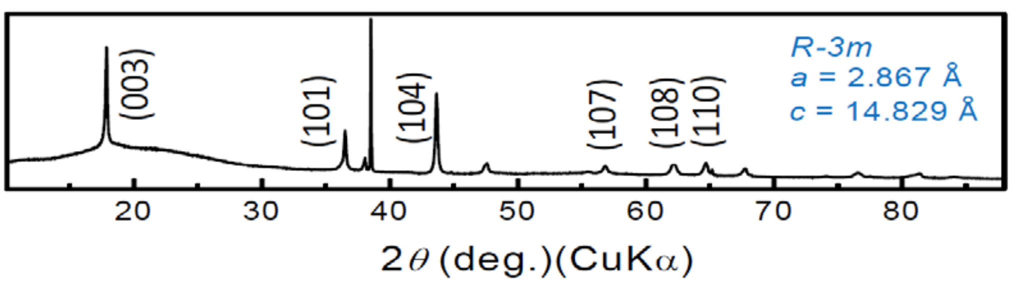
‘c’ ↑

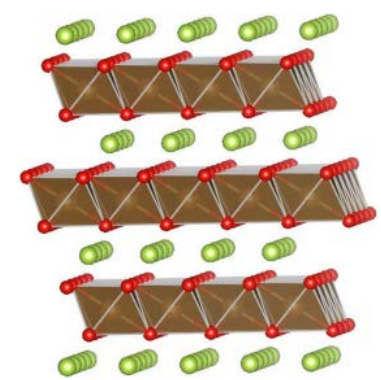
Reversible

In situ X-ray diffraction (XRD) of layered Li_2MoO_3 during the first charge







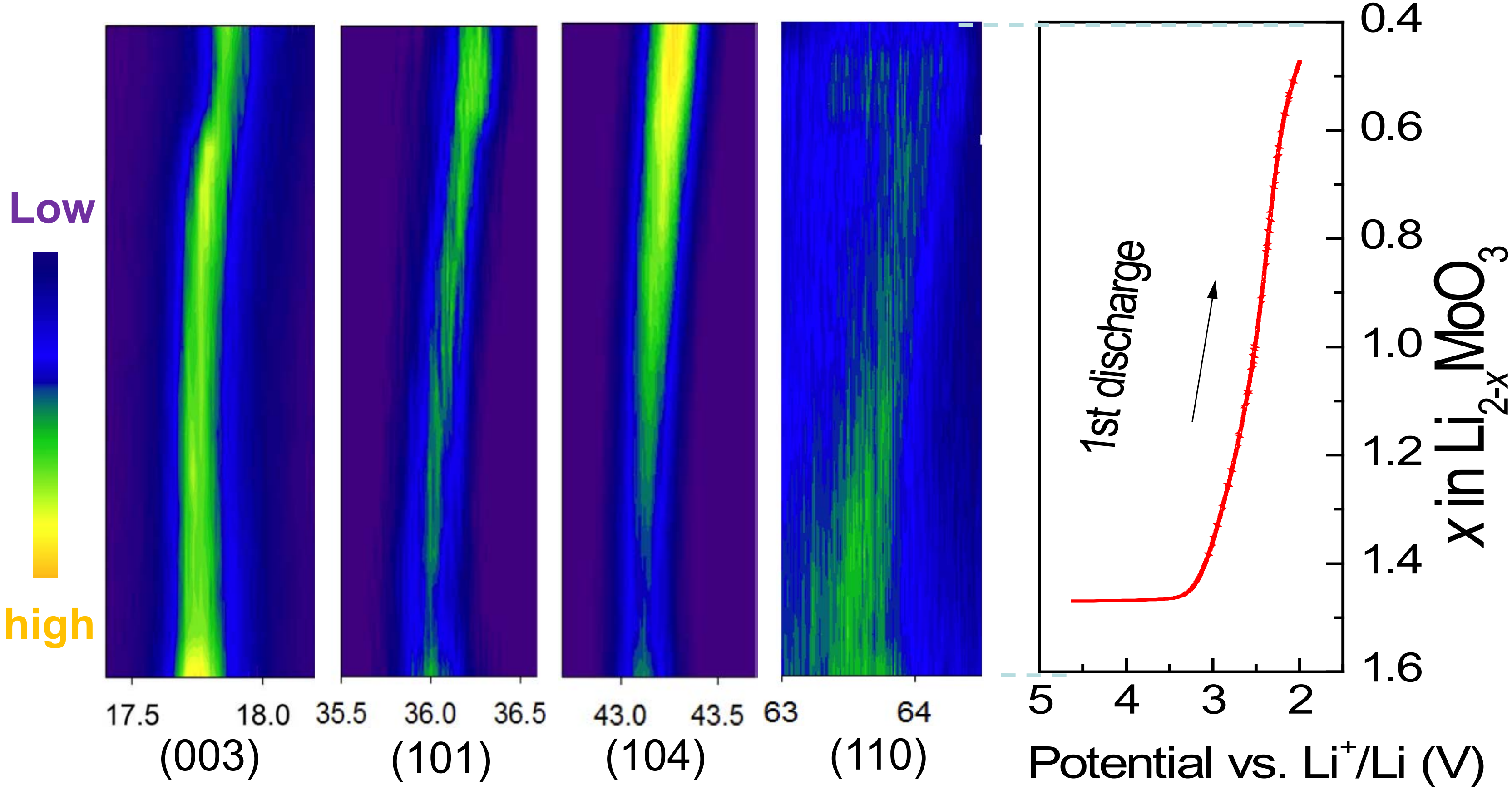


Abnormal expansion in "a" and "b"

The shift of (101) and (110) peaks to the left is in the opposite direction of the "normal" breathing in most of the layer structured cathode materials

Y. N. Zhou et al. ***Nature Communications* 5,** 5381 (2014)

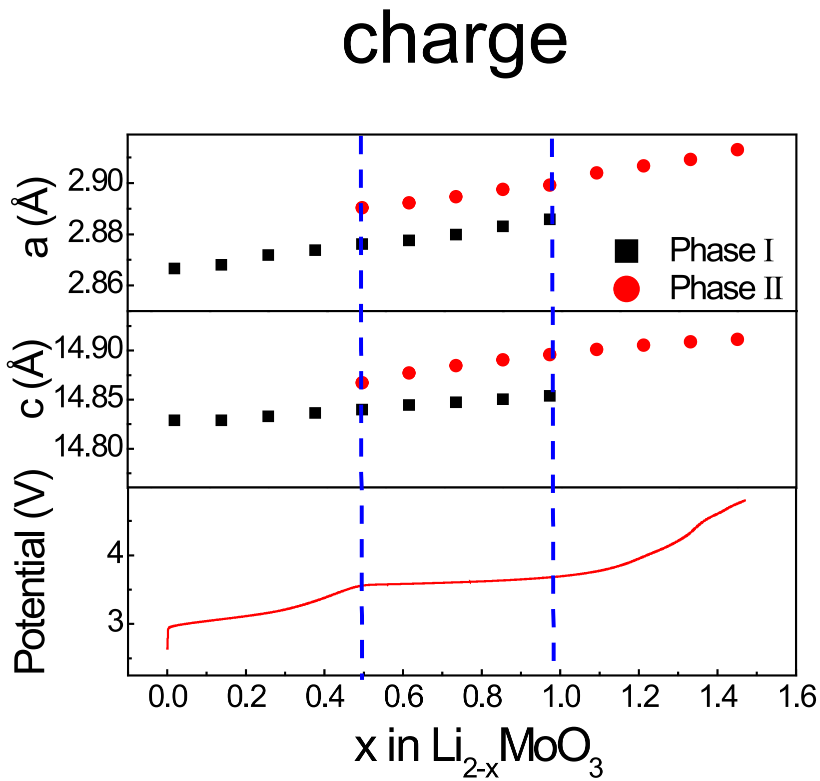
In situ X-ray diffraction (XRD) of Li_2MoO_3 during the first discharge

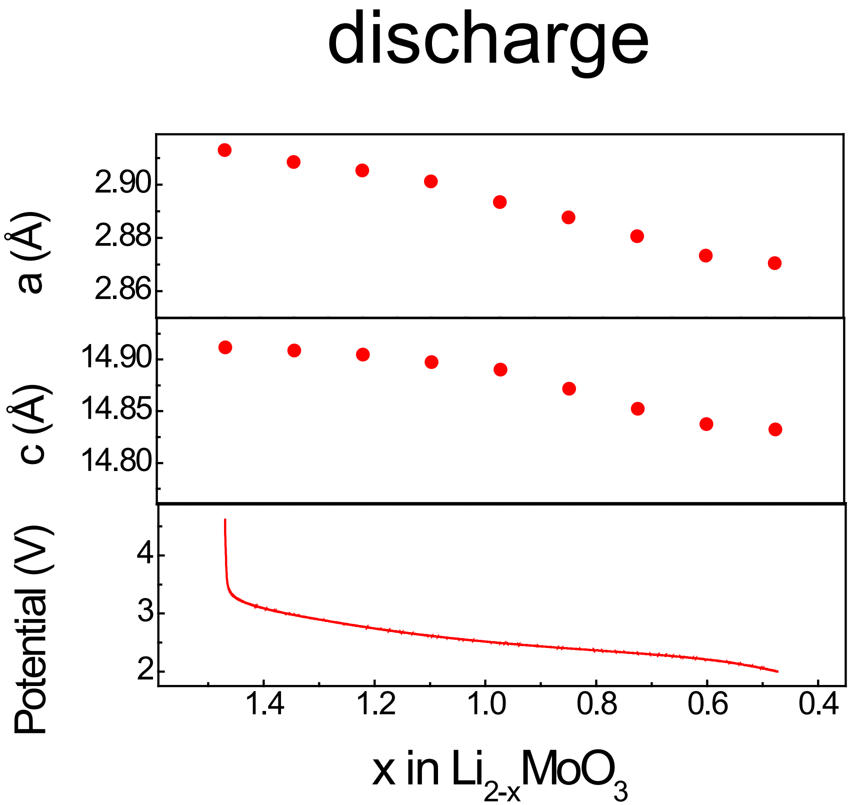


Reversible three-dimension contraction during discharge

Y. N. Zhou et al. ***Nature Communications* 5,** 5381 (2014)

Lattice parameter changes of Li_2MoO_3 during the first charge and discharge





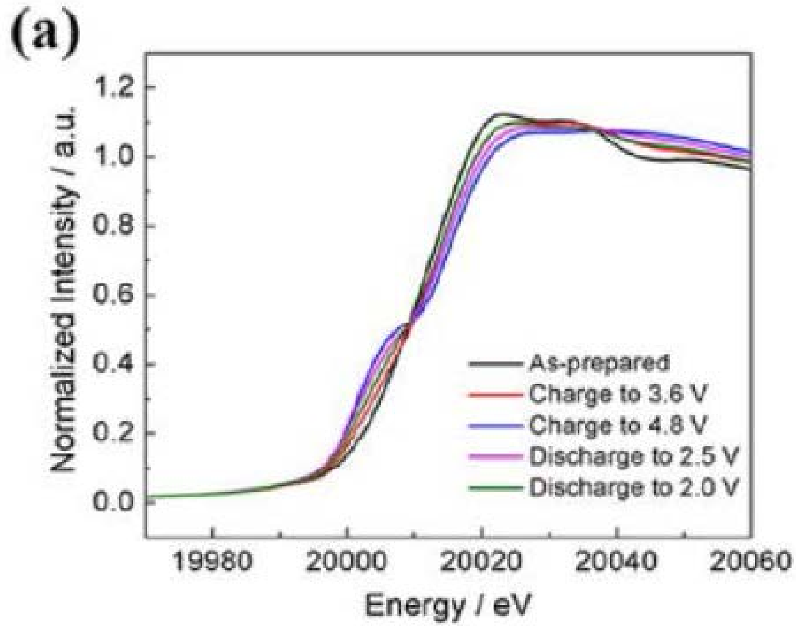
‘*a*’ , ’*b*’ and ‘*c*’ increase during charge

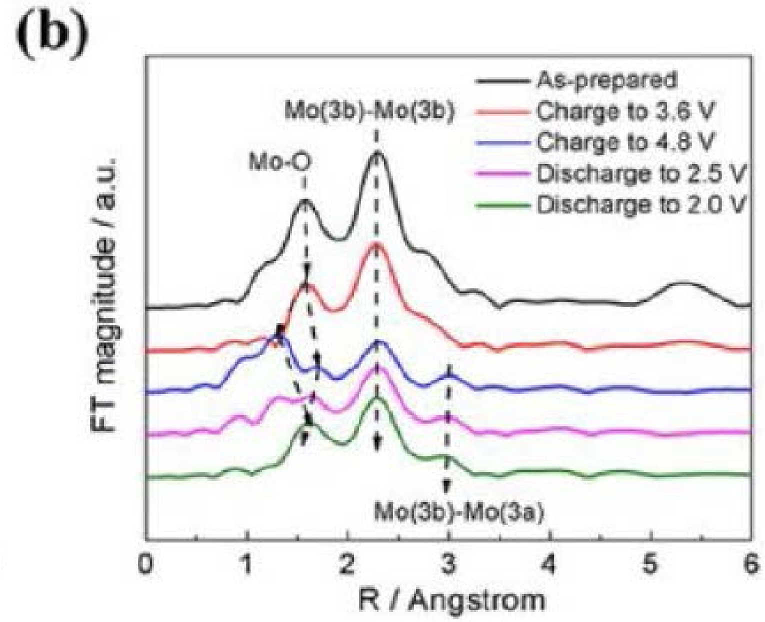
‘*a*’ , ’*b*’ and ‘*c*’ decrease during discharge

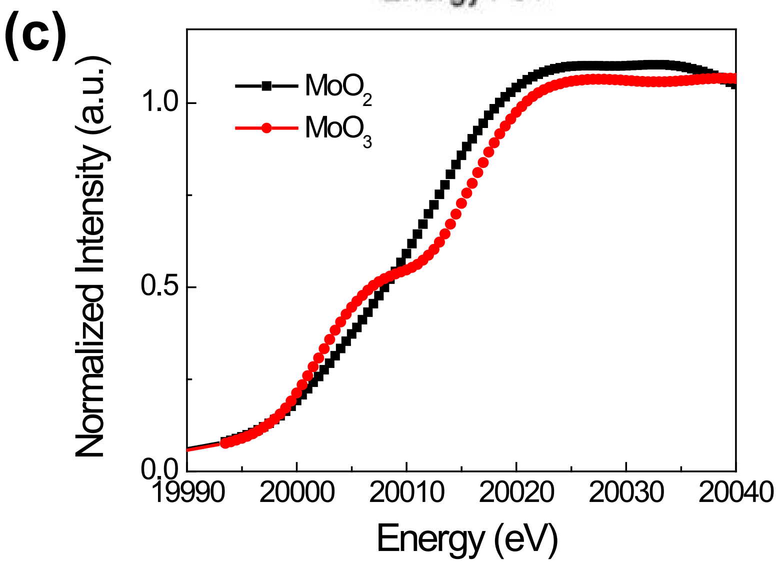
Such three dimensional breathing is in the opposite direction of the ion radius changing during charge-discharge for transition metals

Y. N. Zhou et al. ***Nature Communications* 5,** 5381 (2014)

Ex situ XANES and EXAFS spectra at Mo K-edge of Li_2MoO_3 at different delithiation and lithiation states



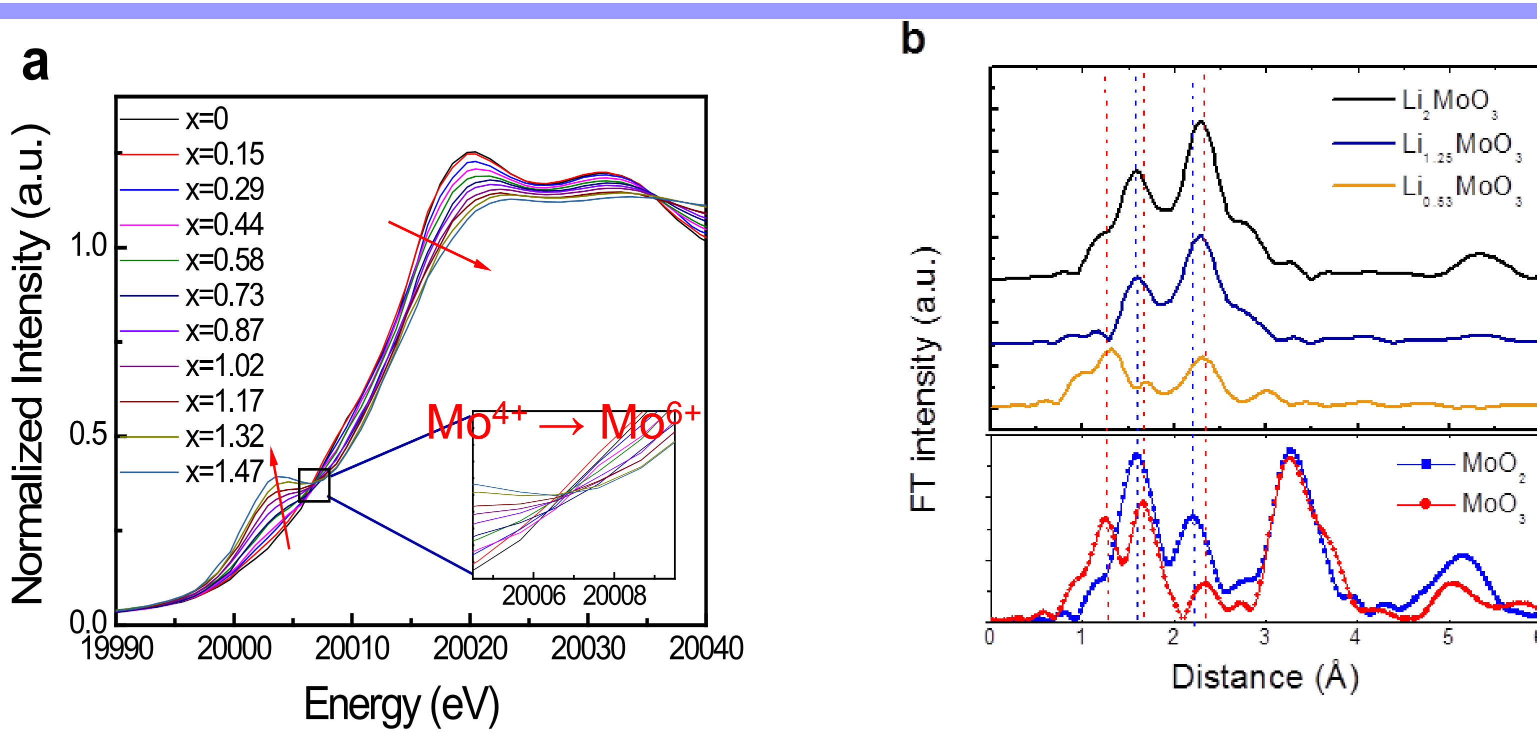




(a) XANES spectra at Mo K-edge of Li_2MoO_3 at different delithiation and lithiation states.
(b) Fourier-transformed Mo K-edge EXAFS spectra of Li_2MoO_3
(c) XANES spectra at Mo K-edge for reference compounds MoO_2 and MoO_3

Results show that Mo was oxidized to Mo^{6+}

In situ x-ray absorption spectra of Li_2MoO_3 during the first charge

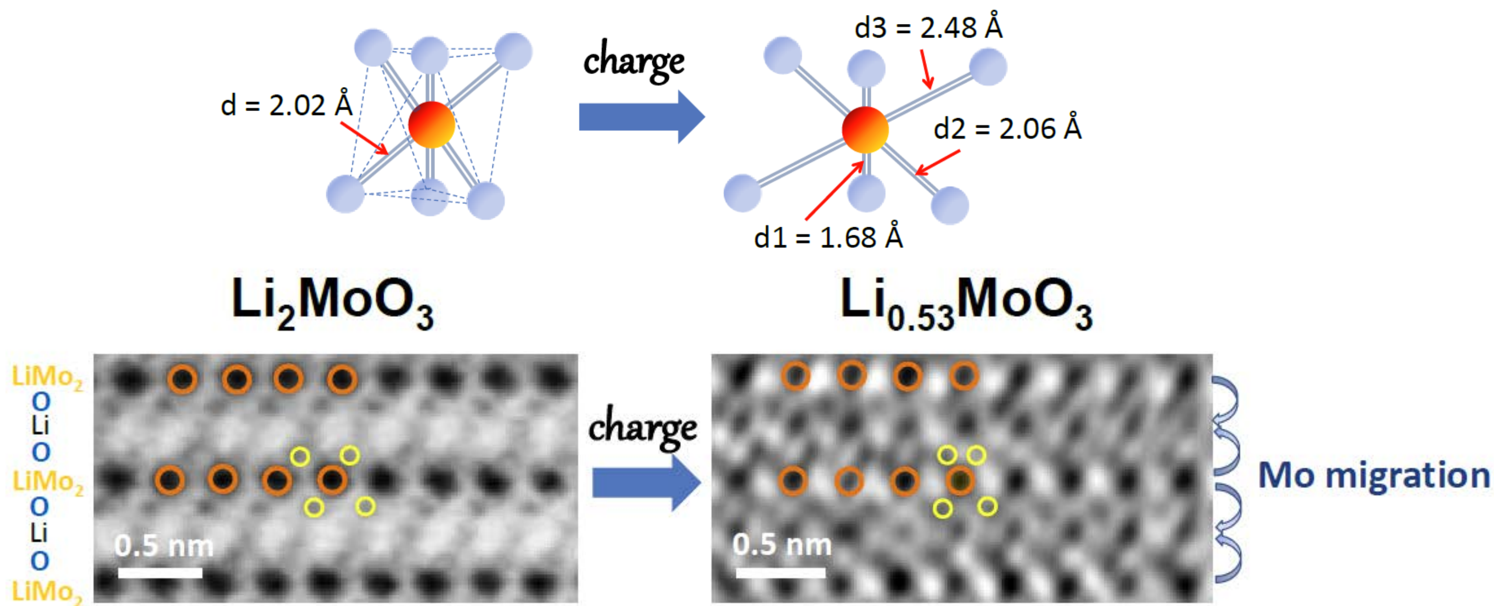


	Path	r (Å)	σ^2 (10^{-3}Å^2)	ΔE (eV)	R
Li_2MoO_3	Mo-O	2.02(3) ± 0.003	4.60 ± 0.32	2.25 ± 1.30	0.004
	Mo-Mo	2.62(6) ± 0.005	9.32 ± 0.38		0.006
$Li_{0.53}MoO_3$	Mo-O1	1.68(4) ± 0.004	10.68 ± 0.25	1.93 ± 0.88	0.002
	Mo-O2	2.06(8) ± 0.005	5.00 ± 0.25		0.004
	Mo-O3	2.48(4) ± 0.003	11.78 ± 0.29		0.013
	Mo-Mo	2.71(2) ± 0.005	4.17 ± 2.6		0.009

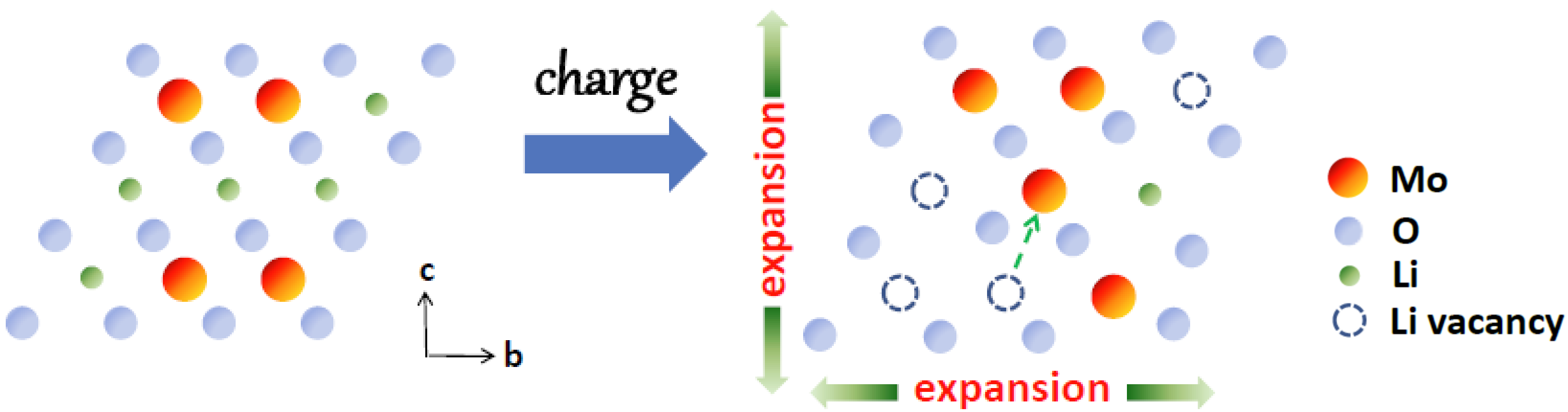
After charging, the uniform Mo-O bond length changed to three different new bond lengths and the Mo-Mo bond length increased

Y. N. Zhou et al. ***Nature Communications* 5,** 5381 (2014)

Structure evolution of Li_2MoO_3 during charge

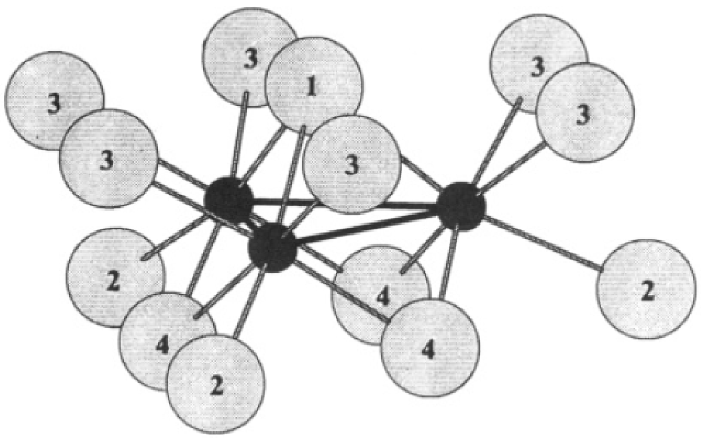


The atomic resolution images obtained by STEM show evidence of the Mo migration to Li layer

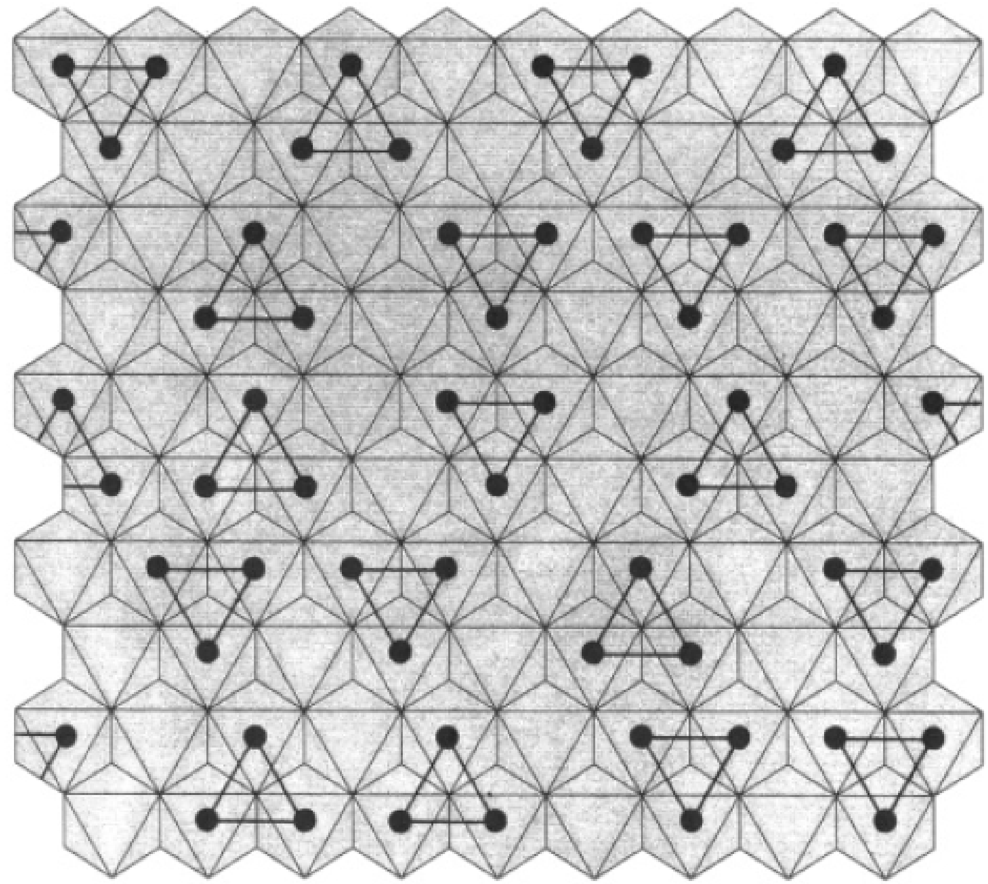


Y. N. Zhou et al. ***Nature Communications* 5,** 5381 (2014)

Mo_3O_{13} cluster model for Li_2MoO_3 described in the literature



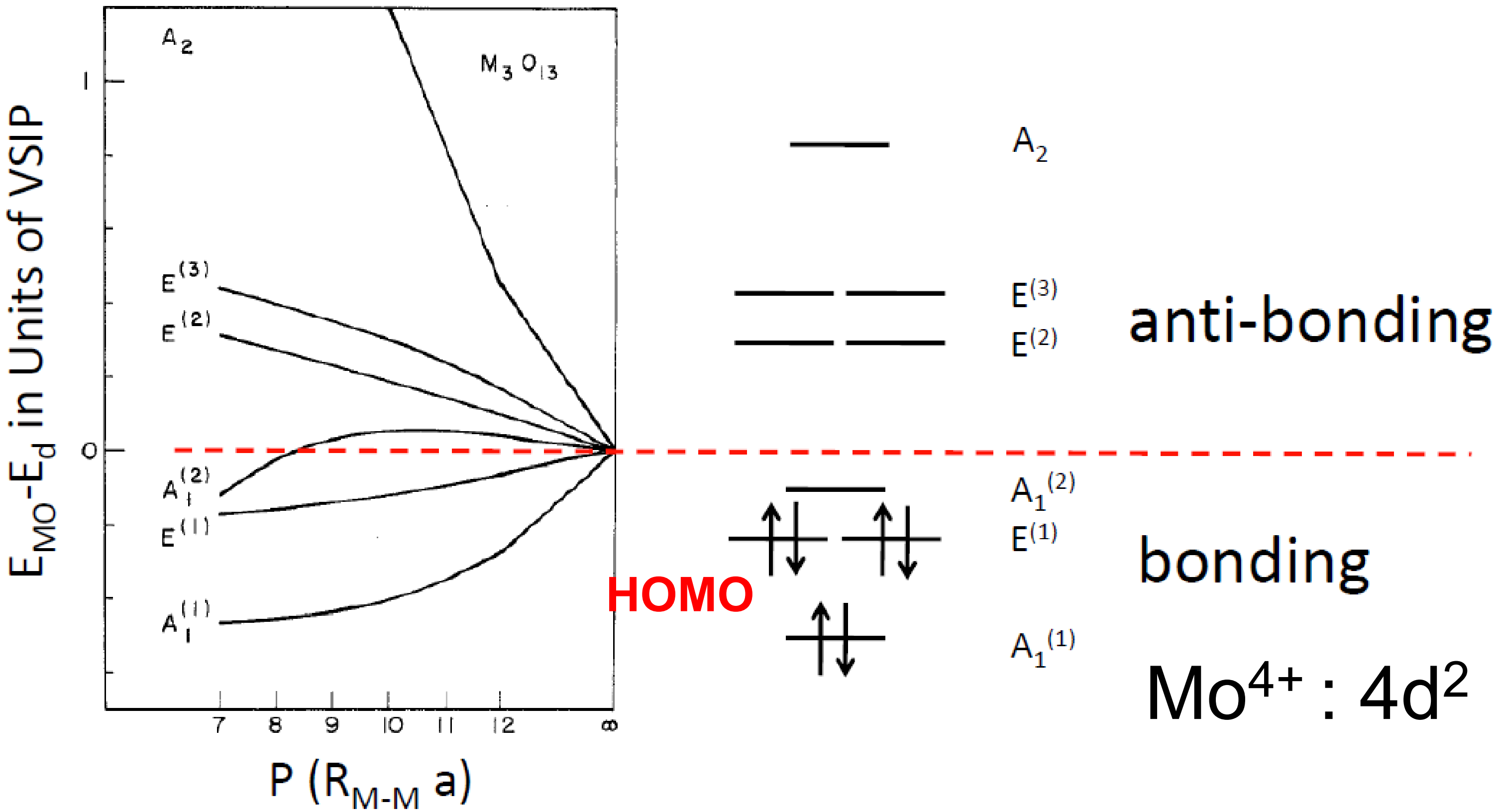
a-b plane



Mo-Mo metal-metal Bonding is the key factor for the “abnormal” breathing in Li_2MoO_3

Hibble S. J., Fawcett I. D., ***Inorg Chem*** 34, 500-508 (1995)

Diagram of the molecular orbital (MO) energies as a function of the orbital exponent for Mo 4d orbitals and the Mo-Mo distance in Mo_3O_{13} cluster



HOMO (highest occupied molecular orbital) is **bonding** orbital
And the removal of the 4d electrons during charging will weaken the metal-metal bonding and cause expansion in ‘a’ and ‘b’

F. A. Cotton, ***Inorganic Chemistry*** 3, 1217 (1964)
Y. N. Zhou et al. ***Nature Communications* 5,** 5381 (2014)

Normal and abnormal lattice parameter changes of layered compounds during delithiation

Cathode materials	Lattice parameter (Å)		Charged phase	Lattice parameter (Å)		Lattice change	
	a	*c*		*a*	*c*	*Δa*	*Δc*
$LiCoO_2$	2.819	14.089	$Li_{0.5}CoO_2$	2.813	14.370	-0.2%	2.0%
$LiNiO_2$	2.883	14.215	$Li_{0.5}NiO_2$	2.820	14.469	-2.2%	1.8%
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	2.87	14.20	$Li_{0.5}$ $Ni_{0.8}Co_{0.15}Al_{0.05}O_2$	2.81	14.52	-2.1%	2.3%
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	2.85	14.18	$Li_{0.5}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$	2.81	14. 46	-1.4%	2.0%
$LiVO_2$	2.840	14.785	$Li_{0.5}VO_2$	2.867	14.53	0.9%	-1.7%
$LiNbO_2$	2.912	10.46	$Li_{0.5}NbO_2$	2.924	10.465	0.4%	0.0%
Li_2MoO_3 (our work)	2.867	14.829	$Li_{0.53}MoO_3$	2.913	14.912	1.6%	0.6%

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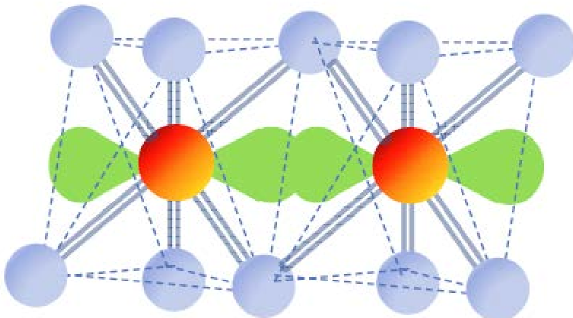
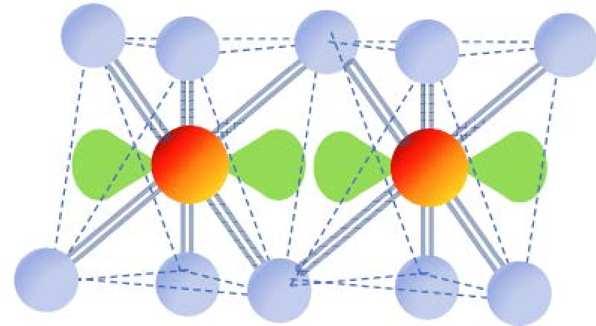
Strength of the M-M bonding in layered compounds for different transition metals in periodic table



t_{2g} orbitals



early transition metal

late transition metal

IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB
scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39
yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41
lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59
lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]

Arrows show the trend to form abnormal breathing oxides

Y. N. Zhou et al. ***Nature Communications* 5,** 5381 (2014)

Response to last year reviewer's comments

Comments from 2014 AMR	Response
The author has been able to develop important collaborations to ensure that key problems of interest to the DOE VTO program have been attacked. The reviewer reported that the closing of the BNL National Synchrotron Light Source will necessitate a revision of the work scheduling until the new light source is available	The collaborations to resolve the key problems of interested to DOE VTO program has be maintained and enhanced. New work schedules to work at other synchrotron facilities at APS at Argonne National Lab and SSRL at Stanford University and ALS at Berkeley have been developed and worked out.,
The reviewer explained that there were some uncertainties about future projects because of the closing of the light source. The reviewer pointed out that for some time it will be necessary for the group to travel to other synchrotrons in order to accomplish new studies; this will require considerably more planning. The reviewer also noted that the development of new collaborators will require careful thought to optimize the collaborative results..	The new planning of using other synchrotron facilities such as APS at Argonne National Lab and SSRL at Stanford University and ALS at Berkeley National Lab. had been developed. The collaboration with scientists at the above facilities have been established, some research quality data had been collected, scientific papers have been prepared or published
The reviewer noted that the PI recognizes that the collaborations need to expand the collaborations with U.S. industry and academic researchers, however and the reviewer agrees with this effort for the future.	The collaborative research with US industrial partners and institutions have been expanded and strengthened.

Collaborations with other institutions and companies

- **Lawrence Berkeley National Laboratory**
  Transitions from Near-Surface to Interior Redox upon Lithiation using high resolution TEM
- **Massachusetts Institute of Technology**
  Transitions from Near-Surface to Interior Redox upon Lithiation using high resolution TEM
- **Drexel University**
  Role of Surface Structure on Li-Ion Energy Storage Capacity of Two-Dimensional Transition-Metal Carbides
- **Oak Ridge National Laboratory**
  long-life lithium-ion battery with a highly porous TiNb2O7 anode
- **Argonne National Lab. (ANL)**
  ***In situ* XRD and XAS study of high energy density Li_2MnO_3-$LiMO_2$ composite (LMR-NCM).**
- **Pacific Northwest National Lab. (PNNL)**
  HR-TEM study of high voltage $LiNi_{0.5}Mn_{1.5}O_4$ spinel cathode materials.
- **Johnson Control Inc.**
  ***In situ* XRD and XAS study of high energy density cathode materials**

- **Beijing Institute of Physics, Chinese Academy of Sciences**
  High energy density cathode material diagnostic studies using atomic level resolution STEM and in situ XRD and XAS

Remaining Challenges and Barriers

- Systematic studies of on the oxidation states and electronic structural changes of Li_2MoO_3 at different charge-discharge states are needed. X-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) at Mo K-edge of Li_2MoO_3 at different charge-discharge states will be good techniques for these studies.
- Three dimensional element mapping of layer structured cathode materials are need as diagnostic tools for Li-ion battery research. Transmission x-ray microscopy technique will be developed for battery research based on the high penetration power of x-ray beam. High voltage spinel material will be a good material for such studies.
- The cycling rate dependent structural changes, especially at high rate cycling are very important for understanding the fundamentals governing the rate capability for high power density batteries for electric vehicle applications. Time resolved XRD and XAS will be good tools for such studies

Proposed Future Work for *FY 2015* and *FY2016*

▣ FY2015 Q3 Milestone:

Continue and complete the x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) studies at Mo K-edge of Li_2MoO_3 at different charge-discharge states..

▣ FY2015 Q4 Milestone:

Continue and complete the preliminary studies of elemental distribution of Fe substituted high voltage spinel cathode materials using transmission x-ray microscopy (TXM).

▣ FY2016 work proposed:

Using time resolved XRD and XAS to study the structural changes at various cycling rates, especially at high rate cycling in order to provide guidance for developing electrode materials with high power density. The widely used commercial layer structured cathode materials will be studied first.

▣ Expand the collaborative research with US academic research institutions and industrial partners.

Summary

- **Relevance**
  - ✓ *Diagnostics study of thermal abuse tolerance (to improve the safety characteristics).*
  - ✓ *Diagnostics study aimed to improve the calendar and cycle life of batteries.*
  - ✓ *Diagnostics study of electrode materials with lower cost potential.*
- **Approaches**
  - *Time resolved X-ray diffraction (TR-XRD) and mass spectroscopy (MS)*
  - *In situ x-ray diffraction and absorption spectroscopy*
  - *Quick x-ray absorption spectroscopy*
  - *High resolution transmission electron microscopy (HR-TEM)*
- **Technical Accomplishments**
  - *Completed thermal stability studies of a series of blended $LiMn_2O_4$ (LMO) -$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) cathode materials with different weight ratios.*
  - *Anew "unit-cell-breathing" mechanism for Li_2MoO_3 during charge-discharge was discovered using synchrotron based XRD and XAS, as well as STEM*
  - *Thermal stability optimized high voltage spinel $LiNi_{1/3}Mn_{4/3}Fe_{1/3}O_4$ was synthesized and characterized*
- **Proposed Future work**
  - *Continue and complete the XAS studies at Mo K-edge of Li_2MoO_3 at different charge-discharge states.*
  - *Continue and complete the studies of elemental distribution of Fe substituted high voltage spinel cathode materials using transmission x-ray microscopy (TXM)*
  - *Using time resolved XRD and XAS to study the structural changes at various cycling rates, especially at high rate cycling*