Battery Materials: Lithium Manganese Spinels

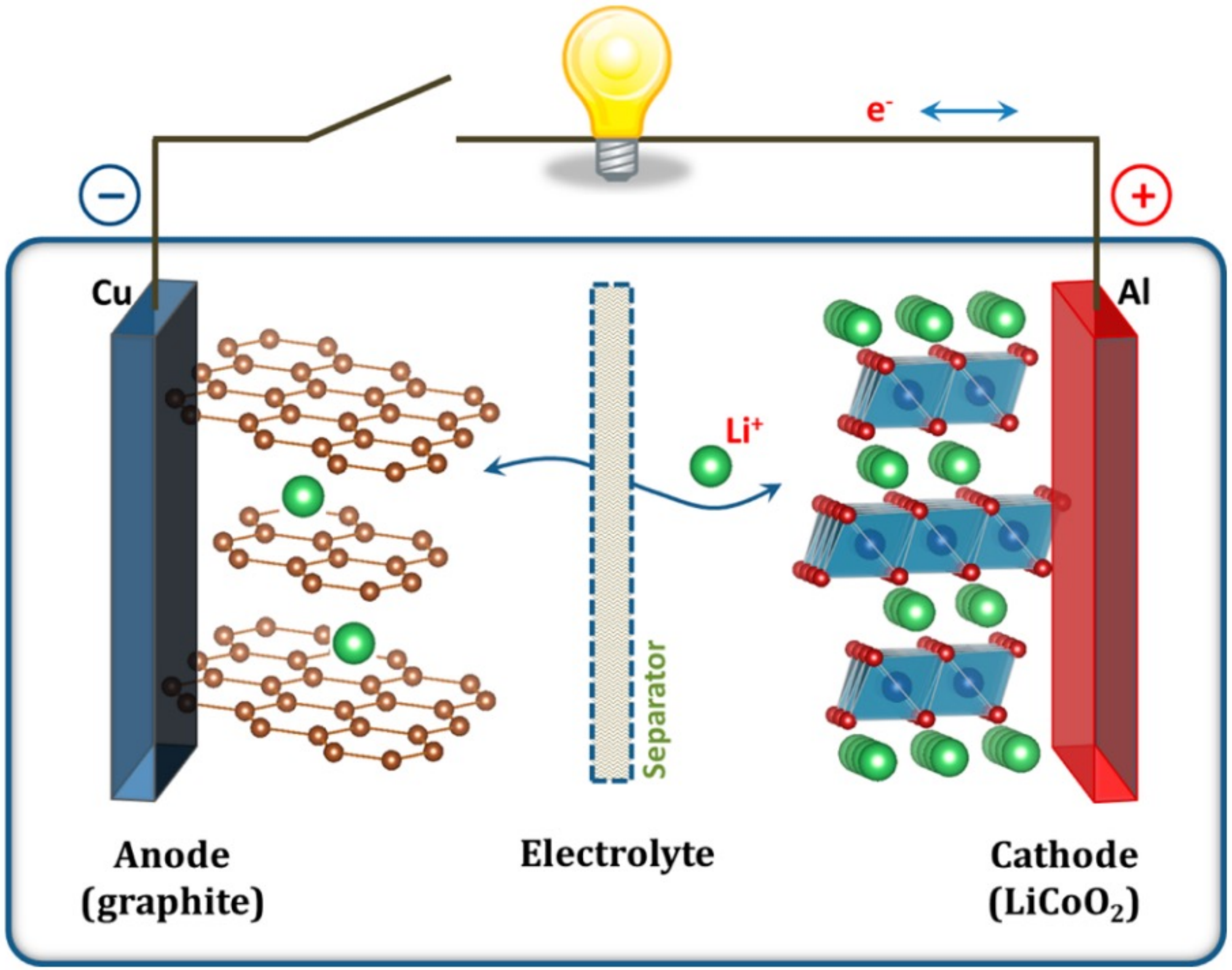
Elizabeth García Ponte

Matrl 286G

Brief battery basics review

- The anode and cathode store Li
- The electrolyte carries Li ions from anode to cathode through a separator
- The free electrons travel through an outer circuit, where they do work

- Structural necessity for cathode: need Li diffusion channels



J. B. Goodenough, K. Park, *J. Am. Chem. Soc.* **2013**, *135,* 1167−1176.

Lithium manganese spinels as cathode materials

- $LiMn_2O_4$
  - Good thermal stability
  - Cost-effective
  - Non-toxic
  - Environmentally friendly
  - Robust crystal structure with fast diffusion kinetics
- Other derivatives:
  - High-voltage spinel cathodes ($LiNi_{0.5}Mn_{1.5}O_4$)
  - High capacity layered Li/Mn rich cathodes
- Spinel structure closely related to layered materials

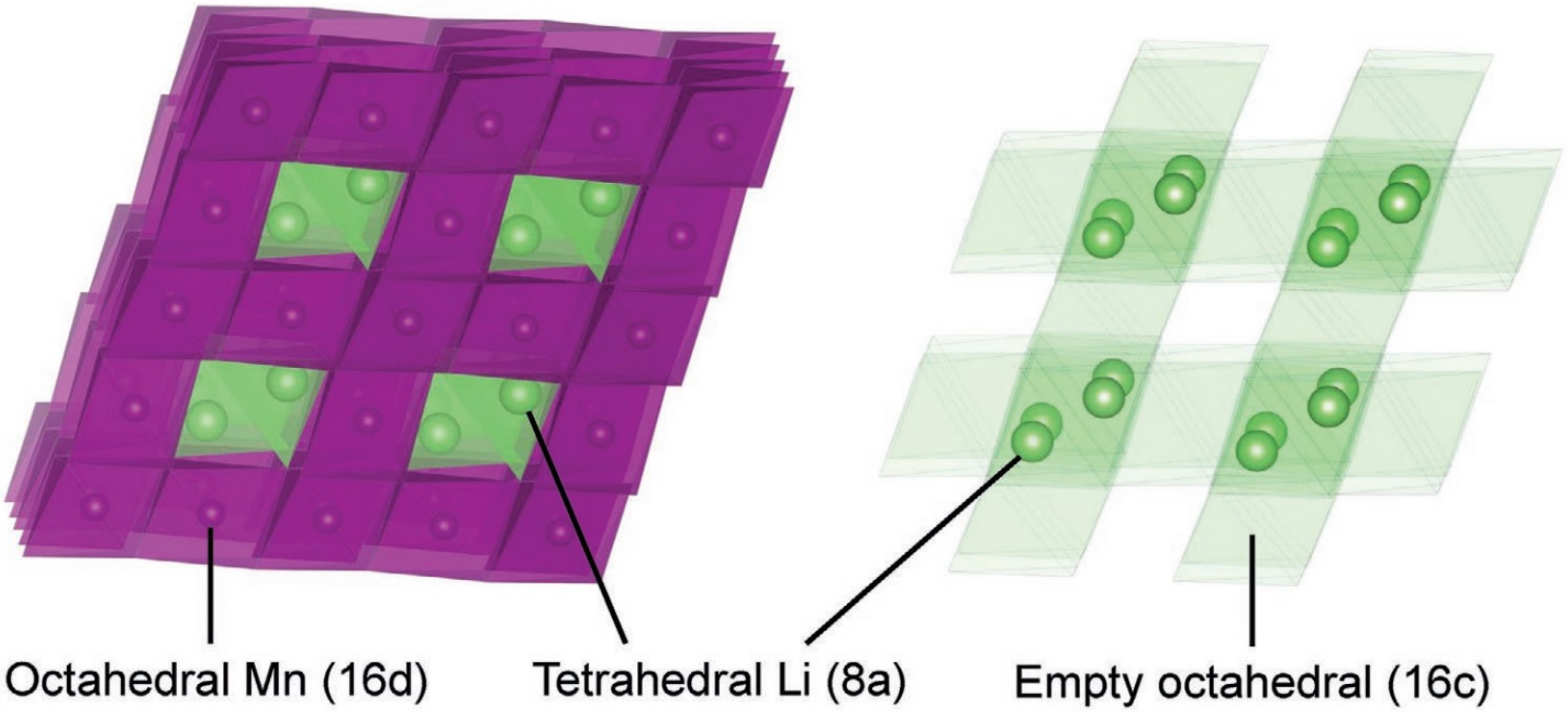
Table 1. Comparison of common cathode materials in LIBs.

Material structure	Composition	Theoretical capacity [mAh g^{-1}]	Capacity at 0.1 C [mAh g^{-1}] (voltage range)	Operating voltage versus Li^+/Li [V]	Specific energy [Wh kg^{-1}]	Co/TM ratio	Cost	Refs.
Spinel	$LiMn_2O_4$	148	120 (3.0–4.3 V)	4.1	490	0	Low	[18]
	$LiNi_{0.5}Mn_{1.5}O_4$	147	125 (3.5–4.9 V)	4.7	590	0	Low	[19]
Layered	$LiCoO_2$	274	185 (3.0–4.45 V)	3.9	720	1	High	[20]
	$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	278	160 (2.8–4.3 V)	3.8	610	0.33	Medium	[21]
	$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$	276	205 (2.8–4.3 V)	3.8	780	0.1	Medium	[21b,22]
	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	279	200 (2.8–4.3 V)	3.8	760	0.15	Medium	[23]
	$Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$	377	240–270 (2.0–4.8 V)	3.6	860–970	0.16	Medium	[24]
Olivine	$LiFePO_4$	170	150 (2.5–4.2 V)	3.4	510	0	Low	[25]
	$LiMn_{0.8}Fe_{0.2}PO_4$	171	160 (2.5–4.2 V)	4.1	650	0	Low	[26]

Y. Huang, Y. Dong, S. Li, J. Lee, C. Wang, Z. Zhu, W. Xue, Y. Li, J. Li, *Adv. Energy Mater.* **2021**, *11*, 2000997

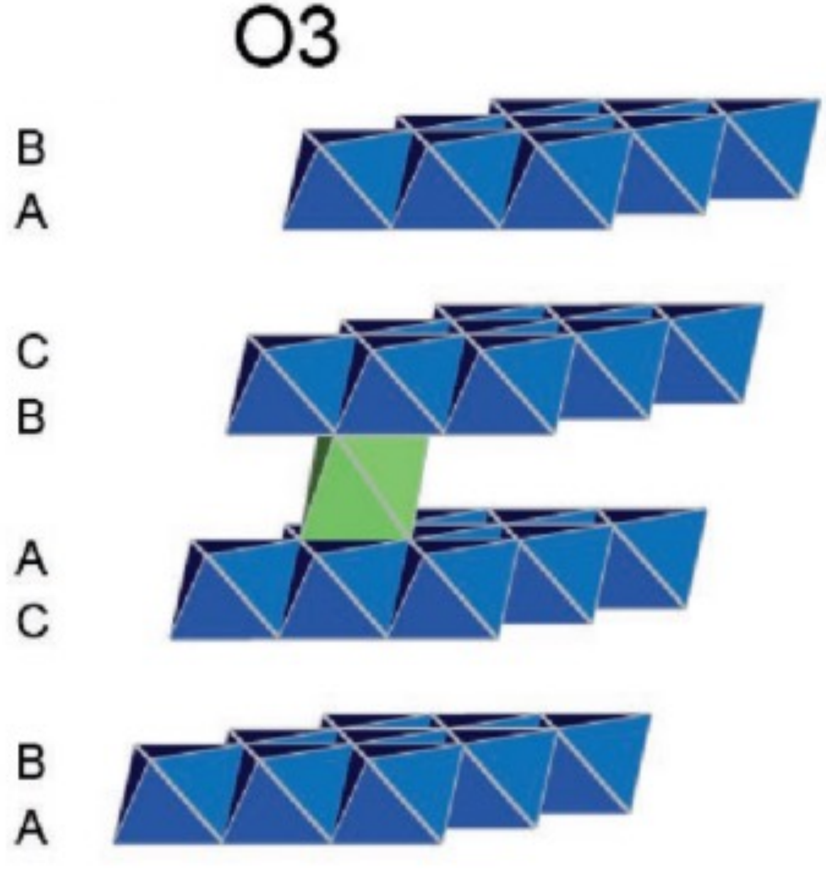
Spinel structure of $LiMn_2O_4$

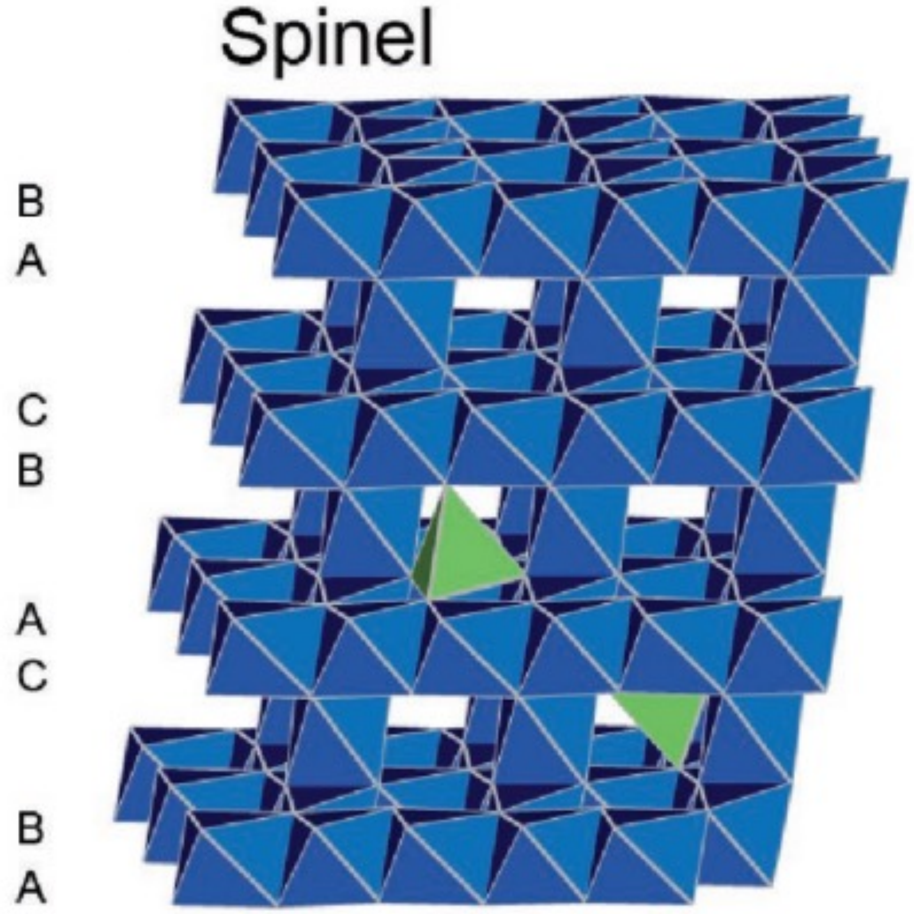
- $A[B_2]O_4$: cubic symmetry
- Space group: $Fd\bar{3}m$



Y. Huang, Y. Dong, S. Li, J. Lee, C. Wang, Z. Zhu, W. Xue, Y. Li, J. Li, *Adv. Energy Mater.* **2021**, *11*, 2000997

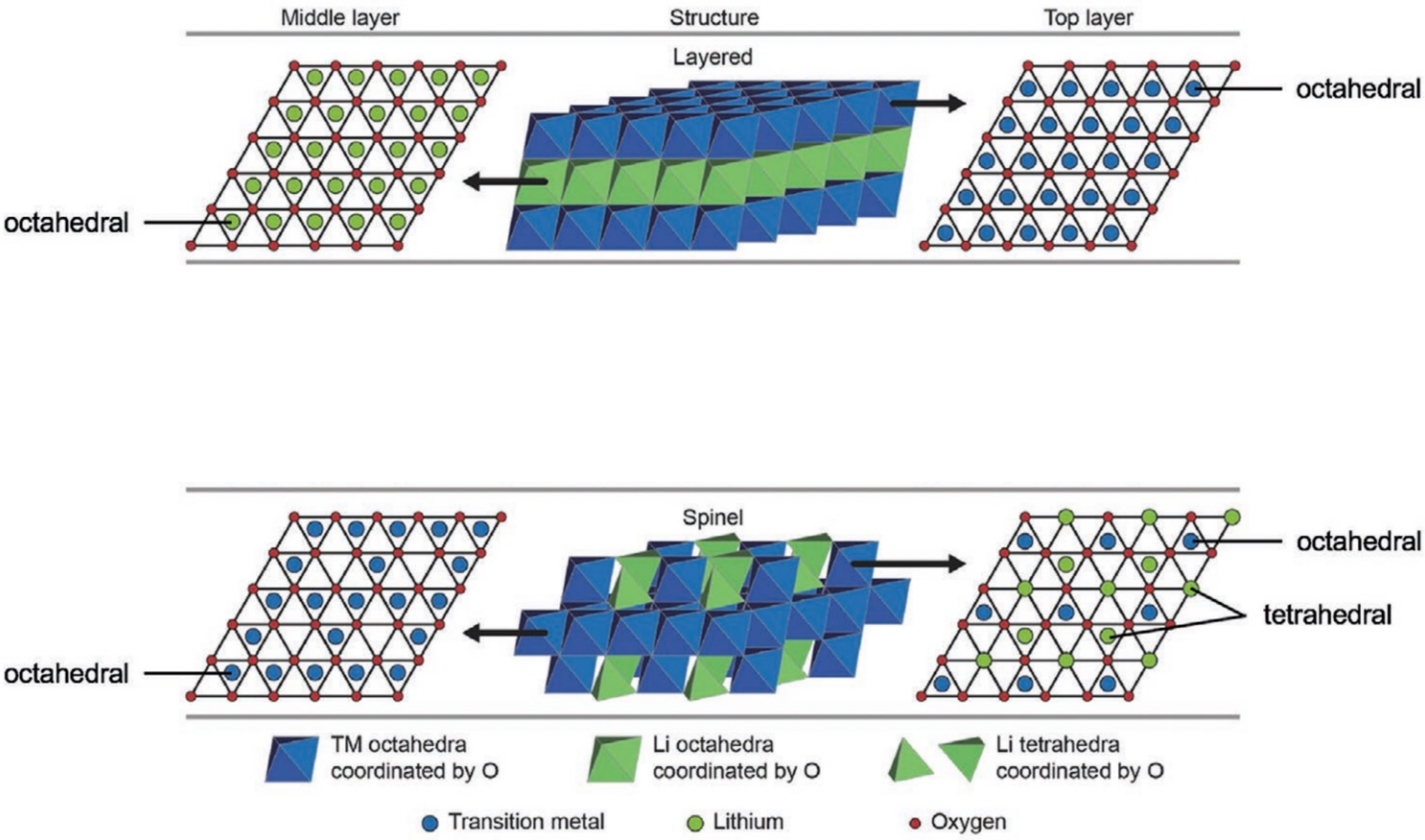
Spinels vs. layered oxides: structural comparison





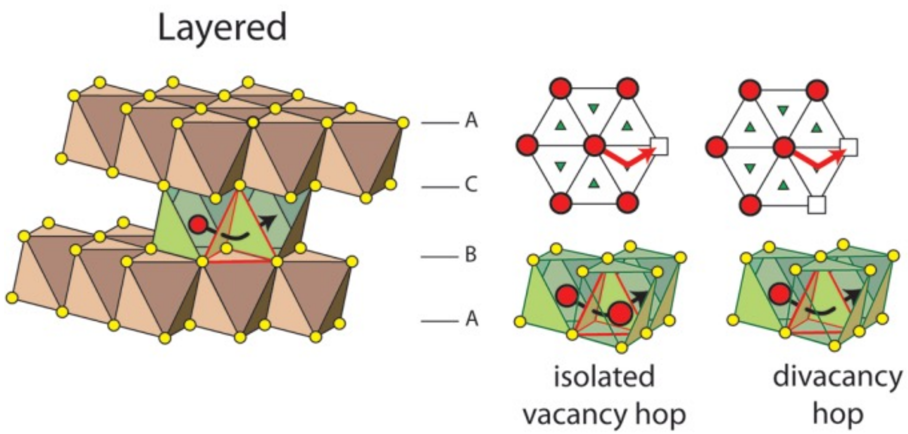
M. D. Radin, S. Hy, M. Sina, C. Fang, H. Liu, J. Vinckeviciute, M. Zhang, M. S. Whittingham, Y. S. Meng, A. Van der Ven, *Adv. Energy Mater.* **2017**, *7*, 1602888

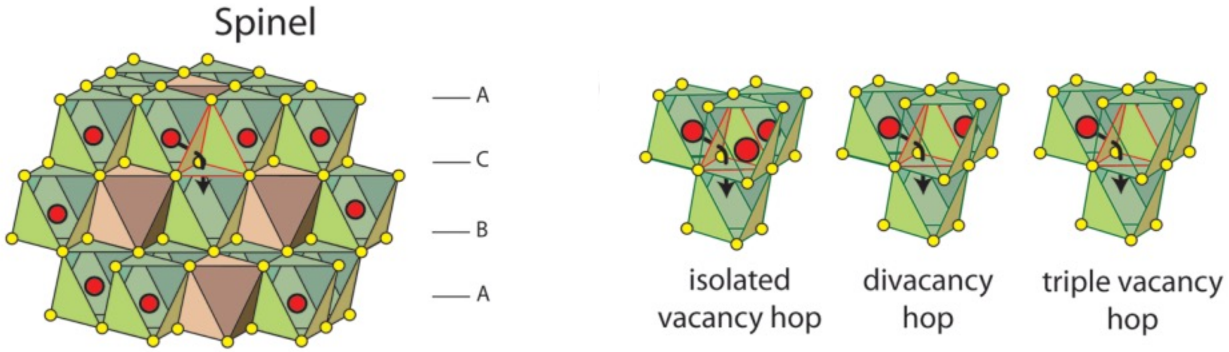
Transformation from layered oxide to spinel

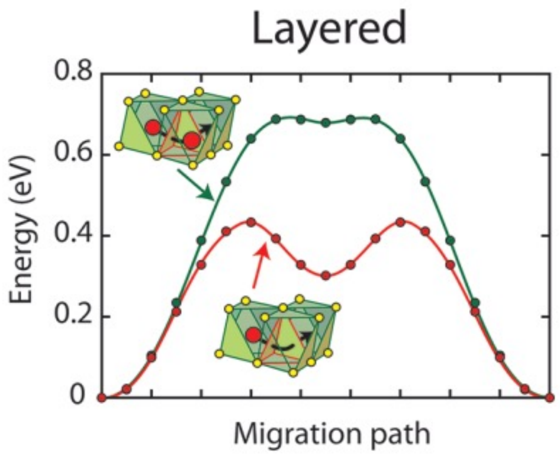


M. D. Radin, S. Hy, M. Sina, C. Fang, H. Liu, J. Vinckeviciute, M. Zhang, M. S. Whittingham, Y. S. Meng, A. Van der Ven, *Adv. Energy Mater.* **2017**, *7*, 1602888

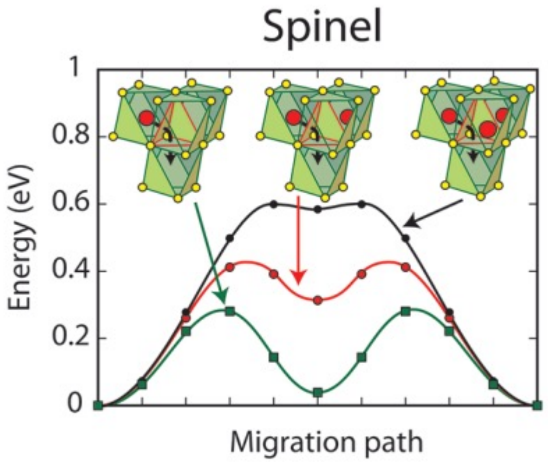
Spinels (x =1) and layered oxides: Li diffusion





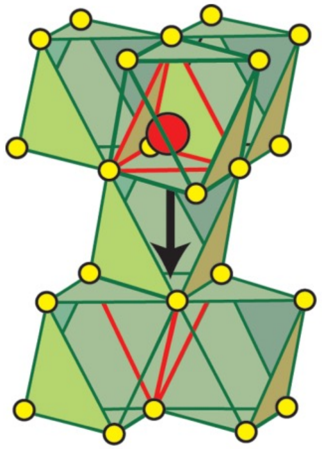


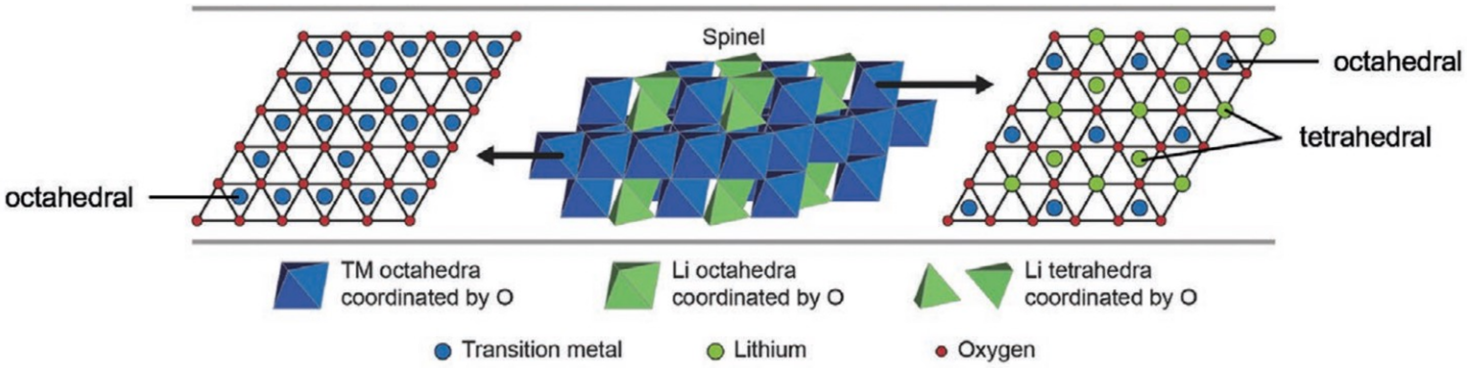
- Li diffusion is driven by Li vacancy clusters
- Diffusion decreases as Li concentration increases



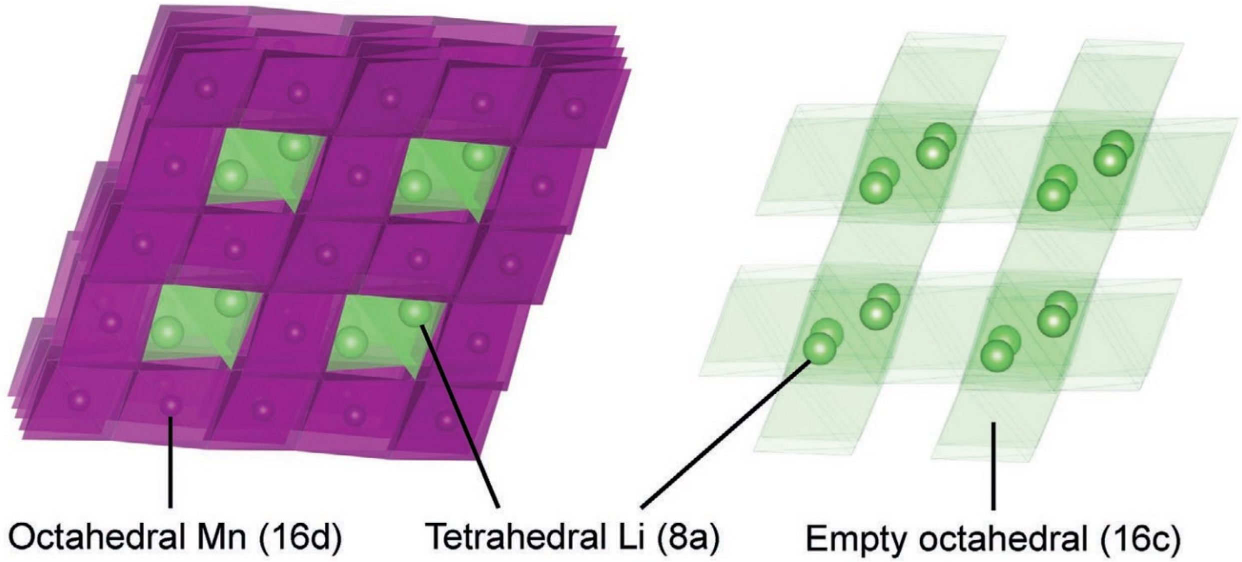
A. Van der Ven, J. Bhattacharya, A. A. Belak, *Acc. Chem. Res.* **2013**, *46,* 1216–1225.

Spinels (x<0.5): Li diffusion



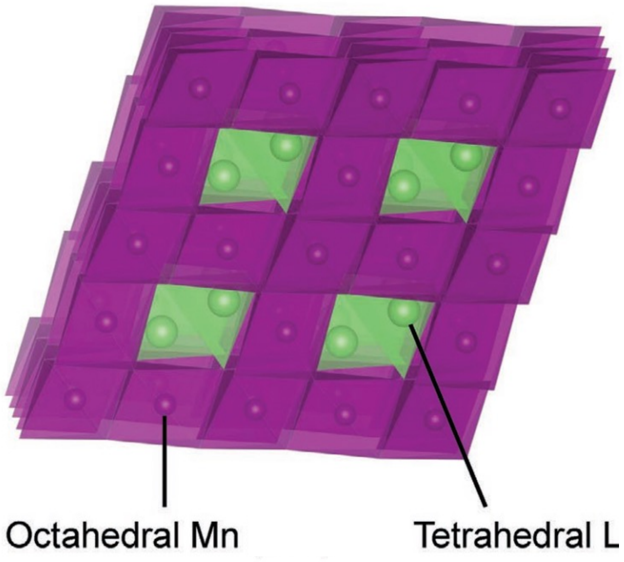


Geometry makes diffusion driven by Li vacancy clusters impossible, so why are diffusion rates so high when x < 0.5?

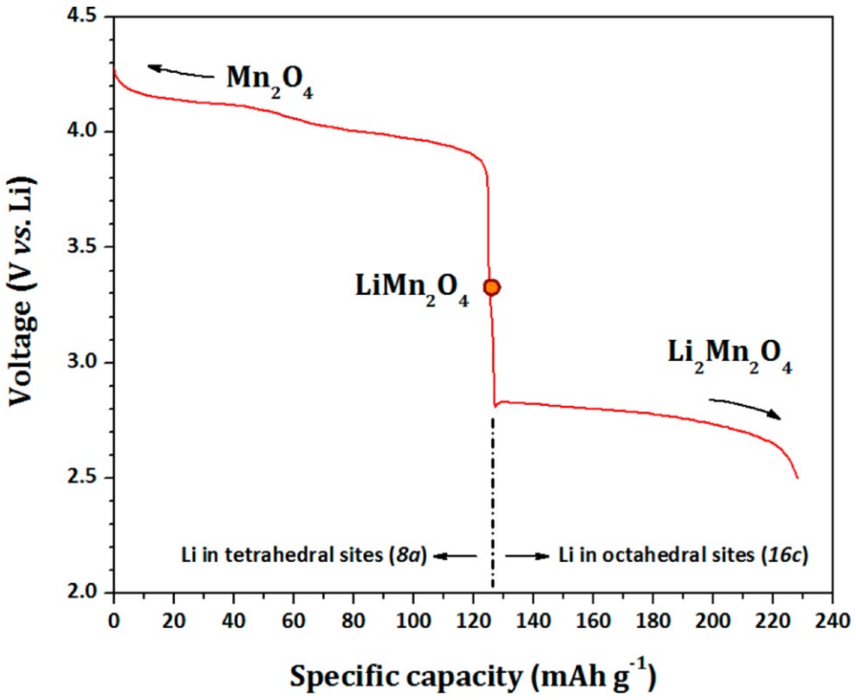


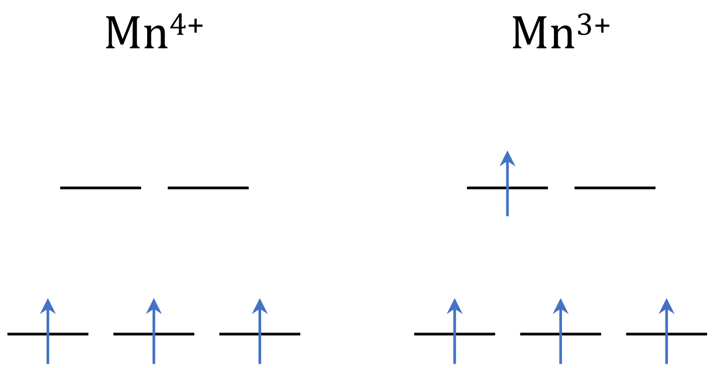
Van der Ven, J. Bhattacharya, A. A. Belak, *Acc. Chem. Res.* **2013**, *46,* 1216–1225.
M. D. Radin, S. Hy, M. Sina, C. Fang, H. Liu, J. Vinckeviciute, M. Zhang, M. S. Whittingham, Y. S. Meng, A. Van der Ven, *Adv. Energy Mater.* **2017**, *7*, 1602888
Y. Huang, Y. Dong, S. Li, J. Lee, C. Wang, Z. Zhu, W. Xue, Y. Li, J. Li, *Adv. Energy Mater.* **2021**, *11*, 2000997

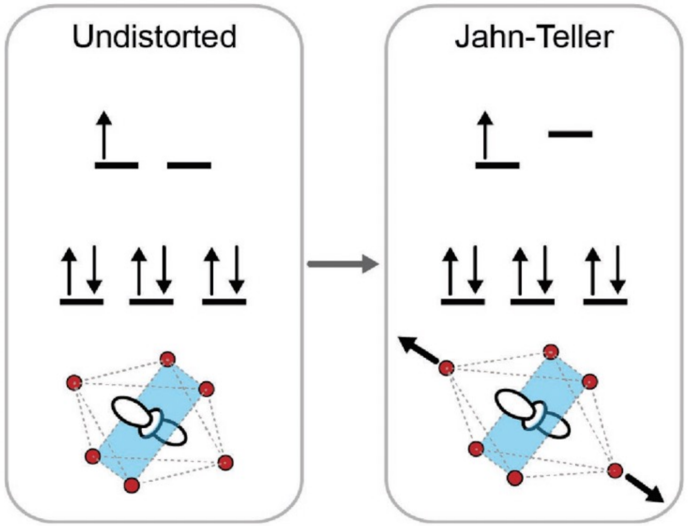
$LiMn_2O_4$: Jahn Teller distortions



Cooperative Jahn Teller distortions at occur with excess Mn (III) and cause two phase plateau.







Y. Huang, Y. Dong, S. Li, J. Lee, C. Wang, Z. Zhu, W. Xue, Y. Li, J. Li, *Adv. Energy Mater.* **2021**, *11*, 2000997
M. D. Radin, S. Hy, M. Sina, C. Fang, H. Liu, J. Vinckeviciute, M. Zhang, M. S. Whittingham, Y. S. Meng, A. Van der Ven, *Adv. Energy Mater.* **2017**, *7*, 1602888
J. B. Goodenough, K. Park, *J. Am. Chem. Soc*. **2013**, *135,* 1167–1176.

$LiNi_{0.5}Mn_{1.5}O_4$: a promising cathode material

- Spinel structure
- Is Co free
- Has a high energy density (650 W hr kg^{-1})
  – 162.5% higher than $LiMn_2O_4$
- High operating voltage ~4.7 V vs. Li
- High thermal stability
- High ionic conductivity

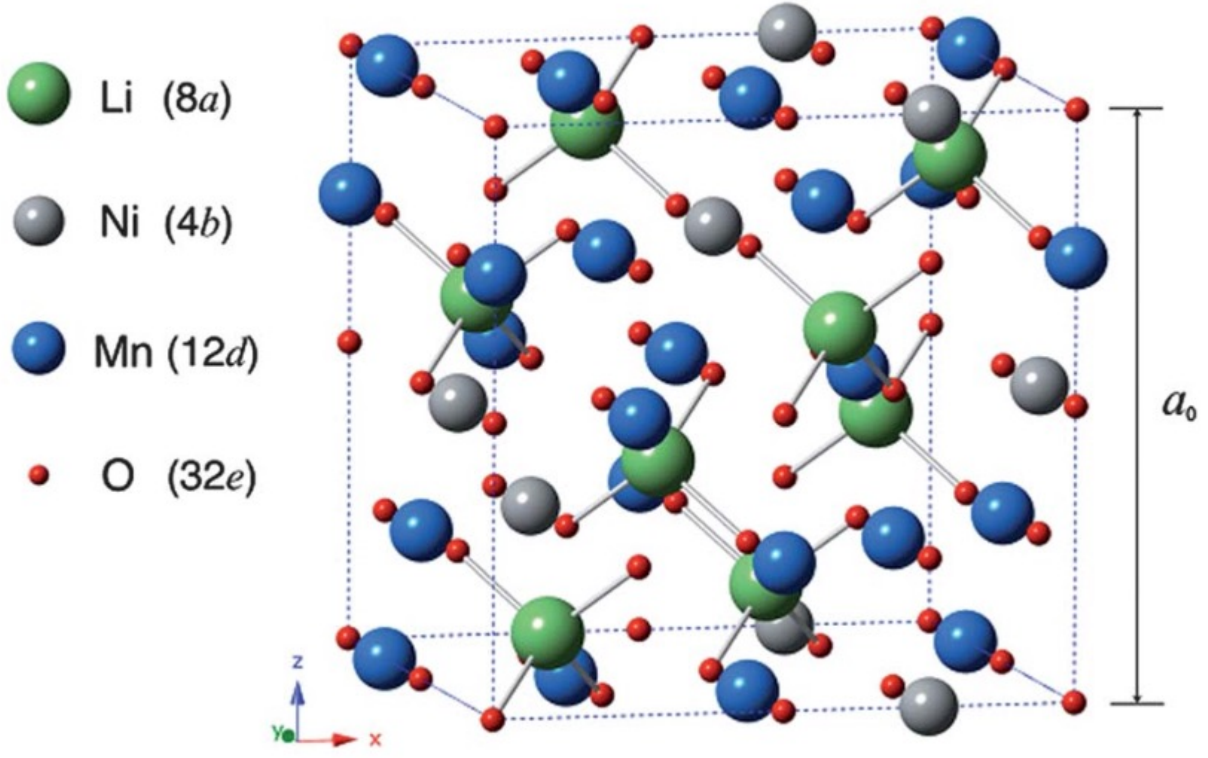
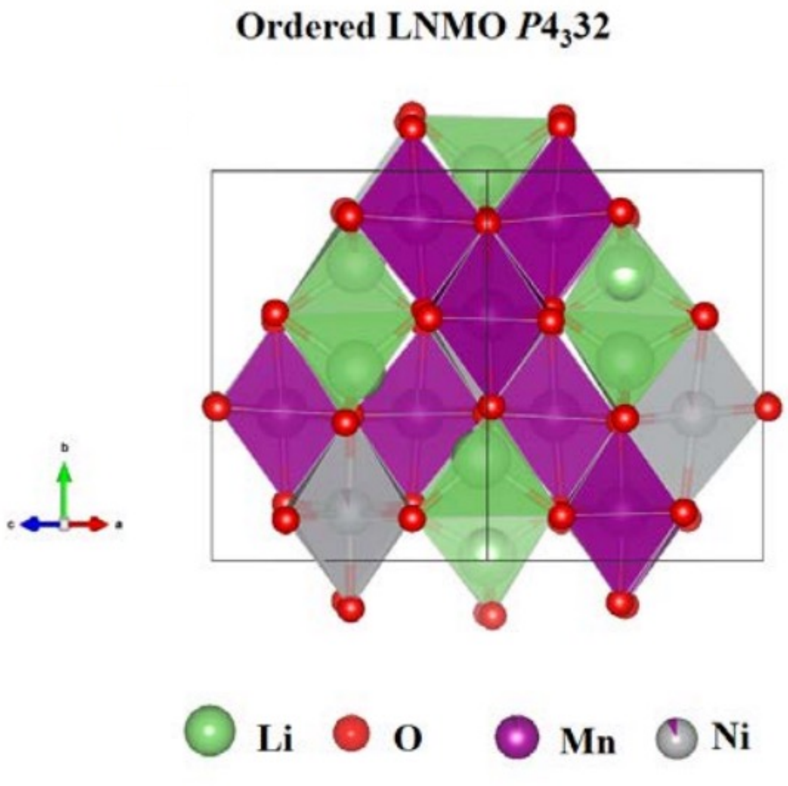
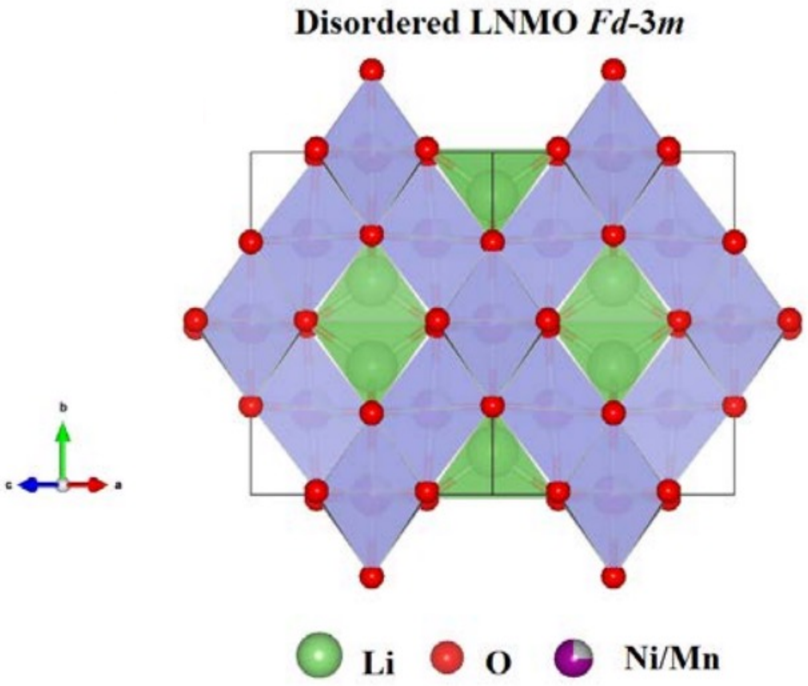


Figure: E. Lee, K. A. Persson, *Energy Environ. Sci.* **2012**, *5,* 6047–6051.
G. Lian, V. K. Peterson, K. W. See, Z. Guo, W. K. Pang, *J. Mater. Chem. A,* **2020,** *8*, 15373–15398

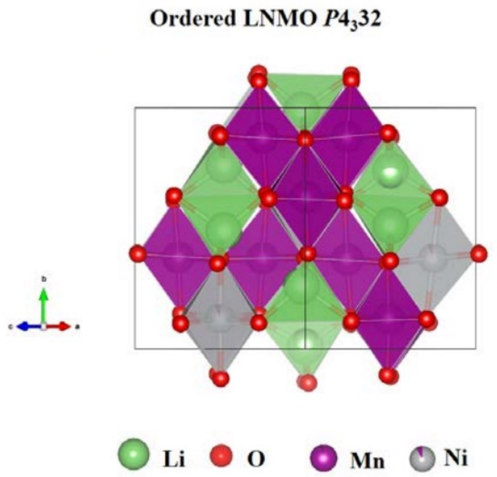
$LiNi_{0.5}Mn_{1.5}O_4$: two different cubic structures

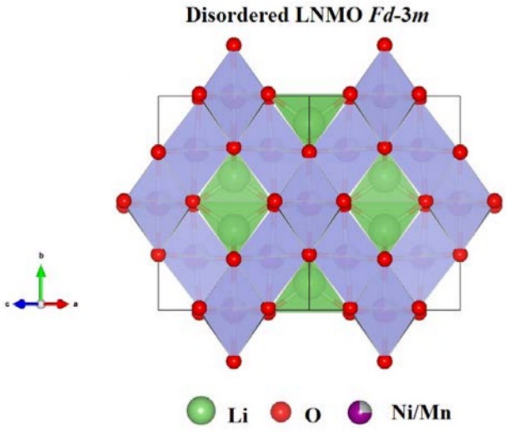


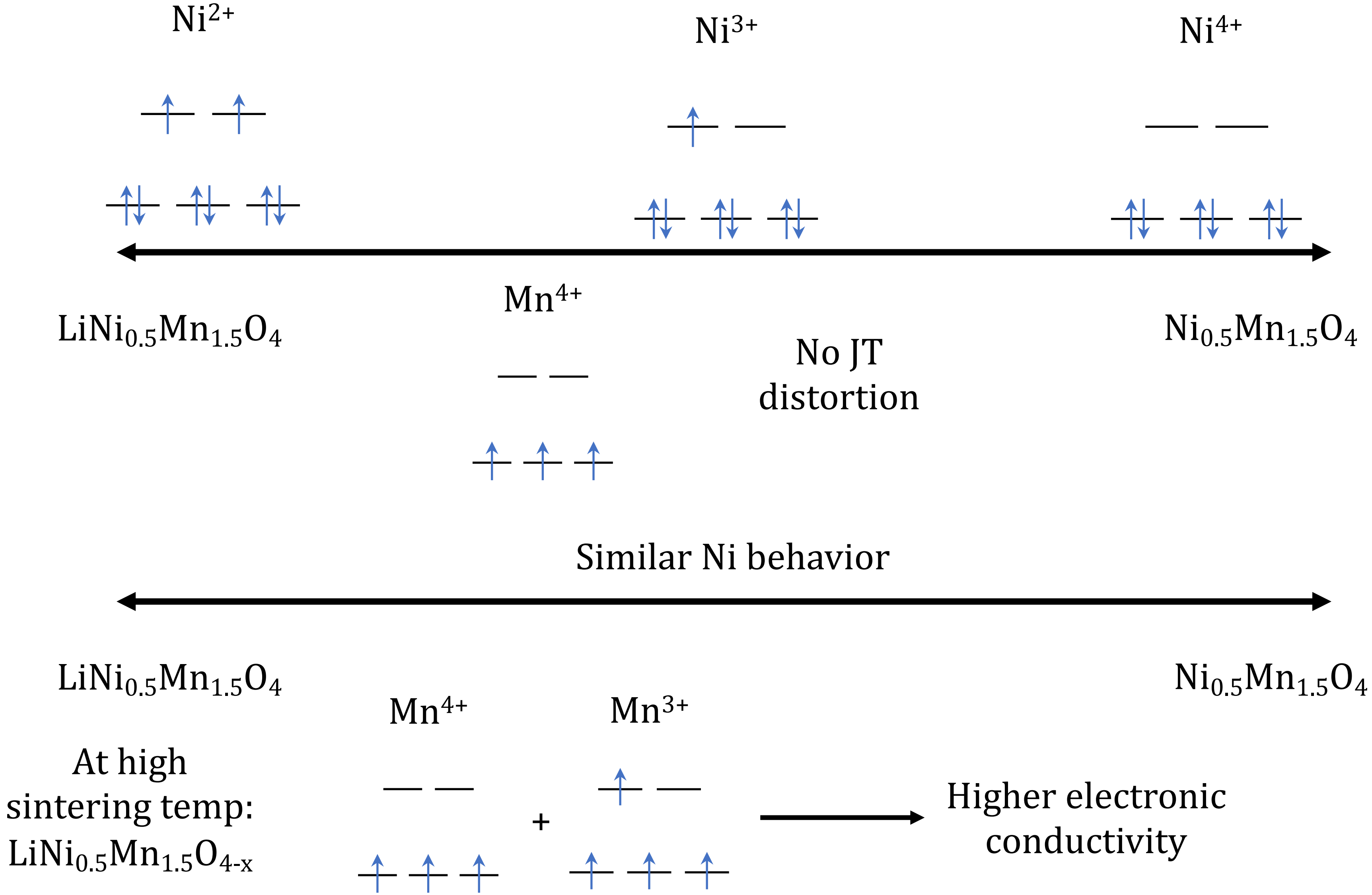


H. Liu, G. Liang, C. Gao, S. Bi, Q. Chen, Y. Xie, S. Fan, L. Cao, W. K. Pang, Z. Guo, *Nano Energy*, **2019**, *66,* 104100.
G. Lian, V. K. Peterson, K. W. See, Z. Guo, W. K. Pang, *J. Mater. Chem. A,* **2020,** *8*, 15373–15398

$LiNi_{0.5}Mn_{1.5}O_4$: redox species

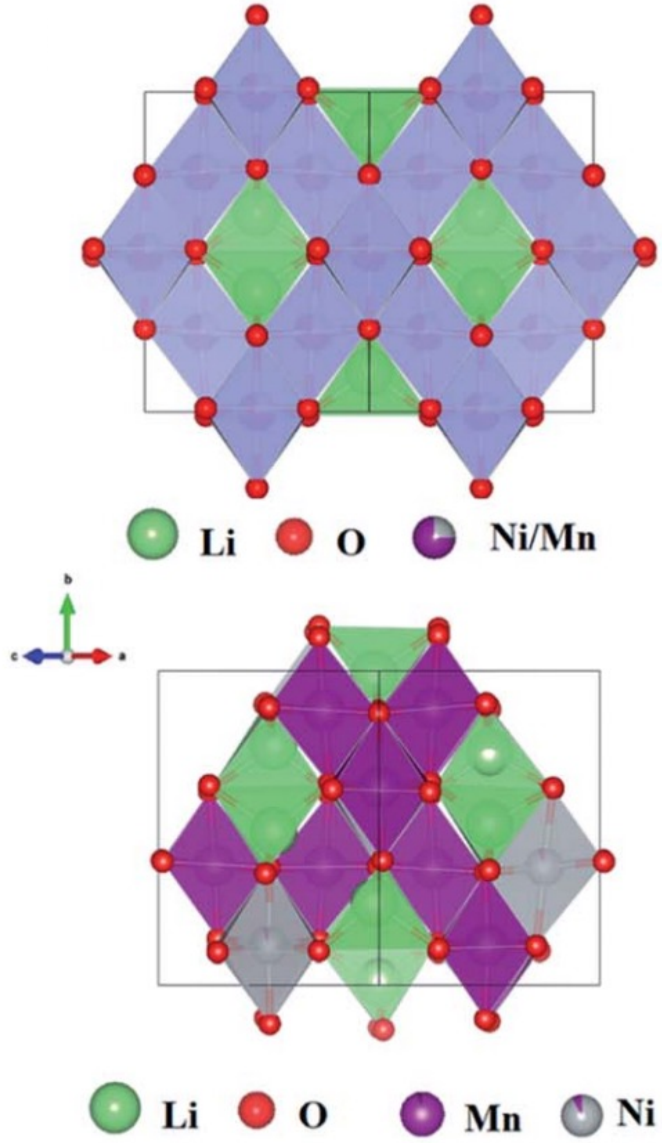


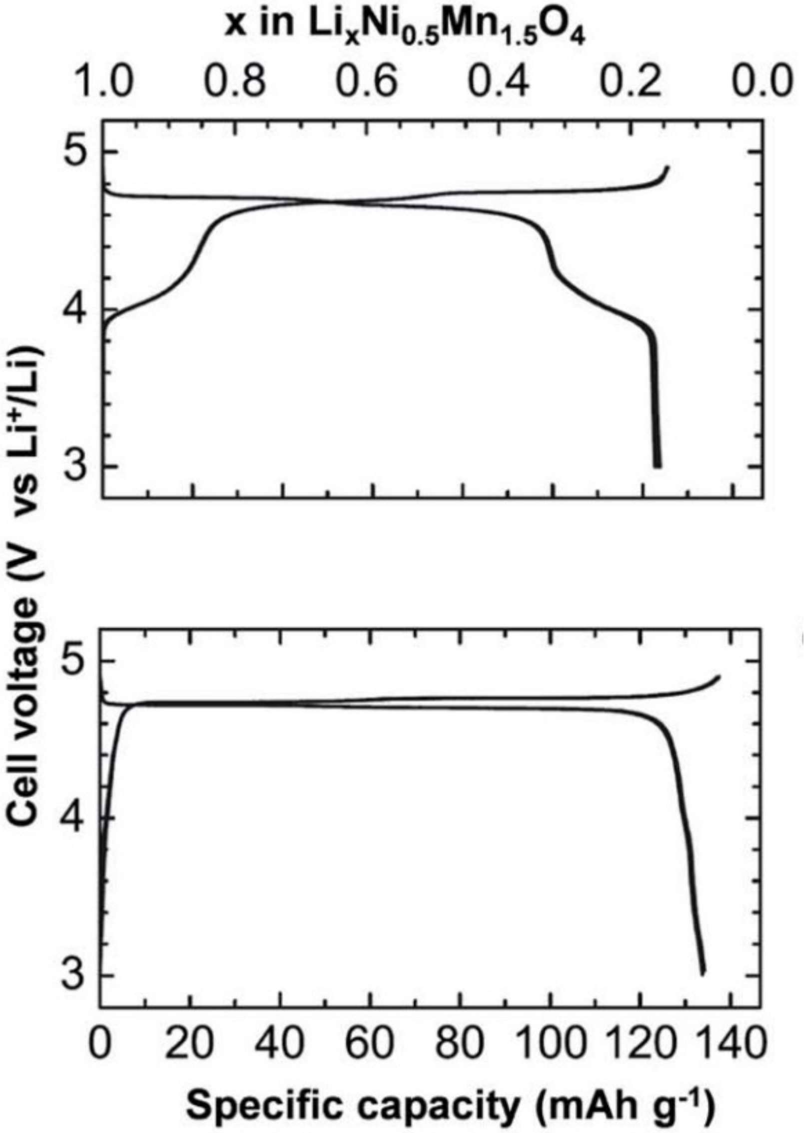




G. Lian, V. K. Peterson, K. W. See, Z. Guo, W. K. Pang, *J. Mater. Chem. A,* **2020**, *8*, 15373–15398
M. Kunduraci, J. F. Al-Sharab, G. G. Amatucci, *Chem. Mater*. **2006**, *18*, 3585–3592

$LiNi_{0.5}Mn_{1.5}O_4$: electrochemical data



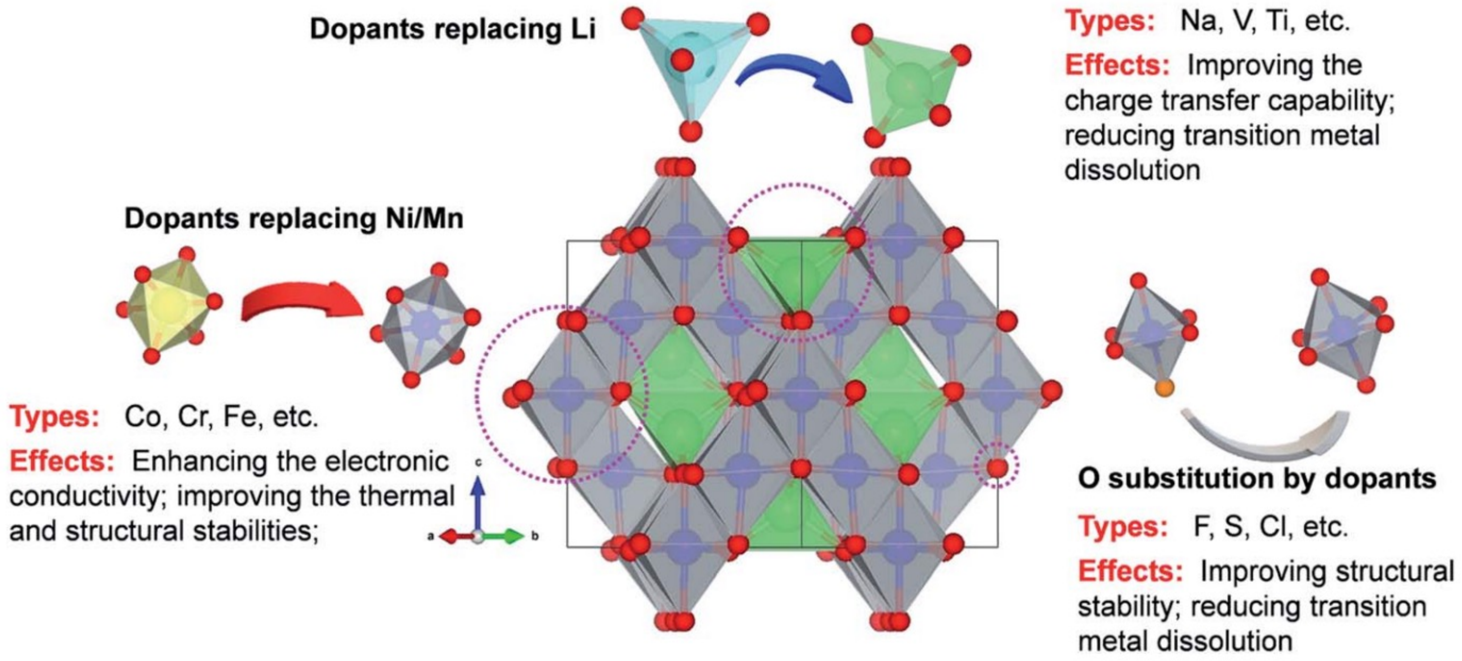


K. Mukai, J. Sugiyama, *J. Electrochem. Soc.* **2010,** *157,* A672-A676.
G. Lian, V. K. Peterson, K. W. See, Z. Guo, W. K. Pang, *J. Mater. Chem. A,* **2020,** *8*, 15373–15398

$LiNi_{0.5}Mn_{1.5}O_4$: some issues and one possible solution

- Problems:
  - Rapid capacity fade
  - Short cycle life
- Causes:
  - Bulk structural and surface chemical instability
  - Lack of suitable electrolyte for high-voltage operation

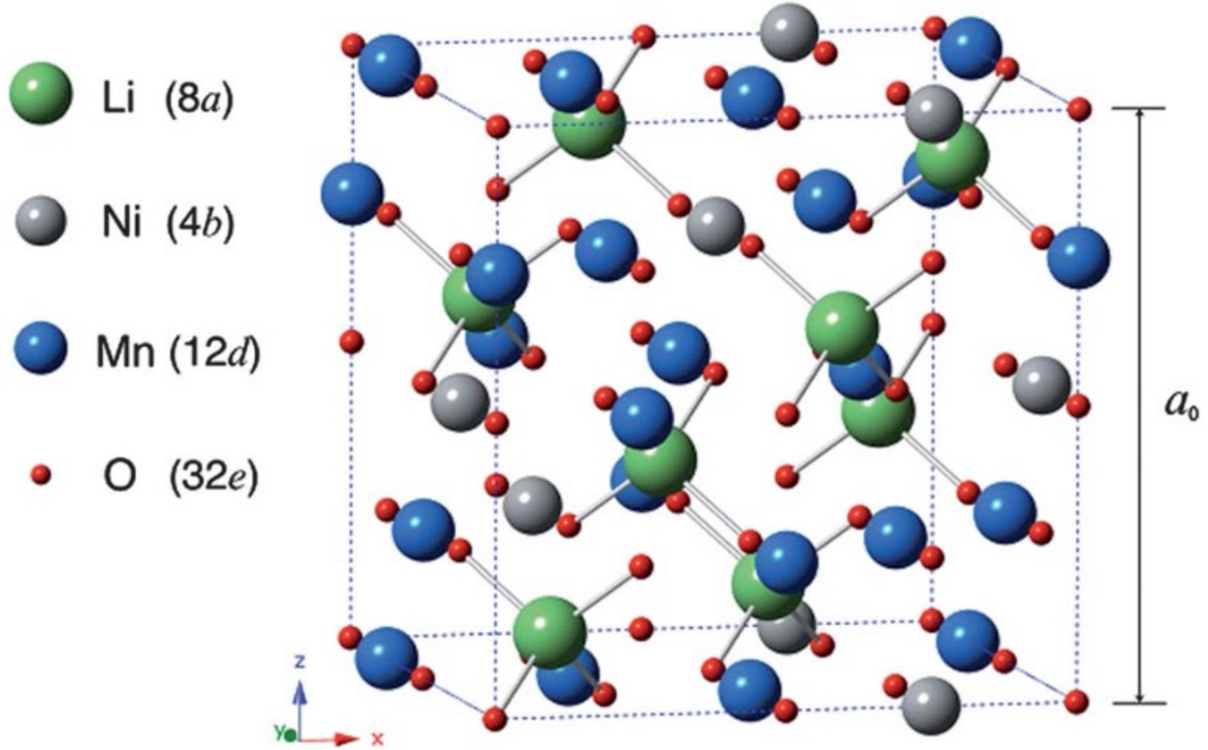
Potential solution:
Elemental doping



G. Lian, V. K. Peterson, K. W. See, Z. Guo, W. K. Pang, *J. Mater. Chem. A,* **2020,** *8,* 15373–15398

$LiNi_{0.5}Mn_{1.5}O_4$: my research interests

- Understand the magnetic ground states
  - What are the driving forces making one more favorable than another?
- Calculate Mn-Mn, Mn-Ni, Ni-NI J couplings
  - Cluster Expansions
  - Monte Carlo simulations
- Assistance in EPR interpretation



Questions?