

(Grand Challenges of Energy Science)
Disordered Cathode Materials for Li-Ion Batteries

Alexander Urban, Dong-Hwa Seo, Jinhyuk Lee,
Aziz Abdellahi, and Gerbrand Ceder

*Department of Materials Science and Engineering,
University of California, Berkeley.*

aurban@berkeley.edu

Berkeley, CA, April 13, 2017

Li-ion batteries have enabled a technological revolution

Li-ion batteries made possible

- Modern portable electronics
- Electric vehicles

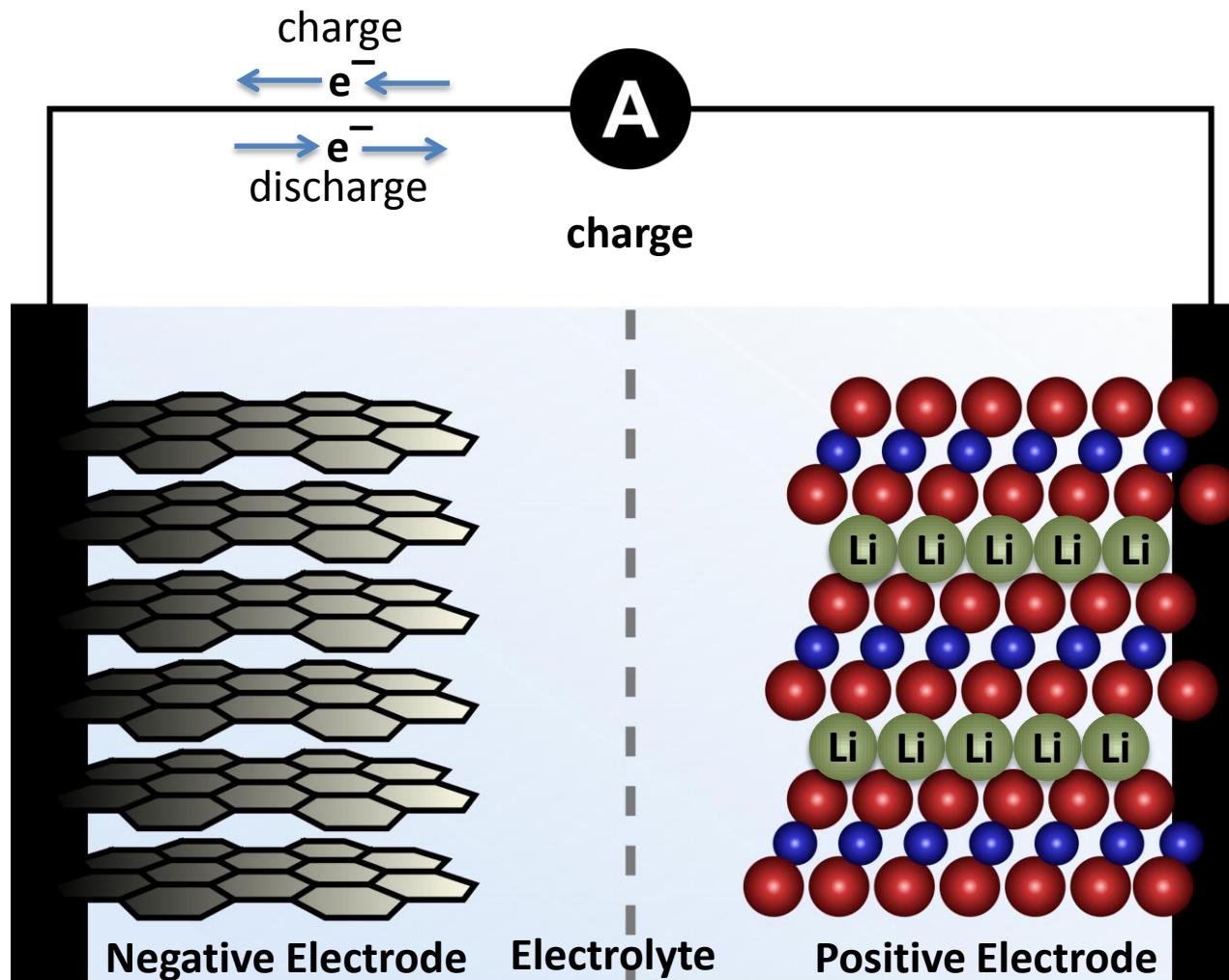


Huge demand for better LIBs

- Make smartphones last longer/more powerful
- Increase range of EVs



Li-ion batteries function by shuttling Li ions



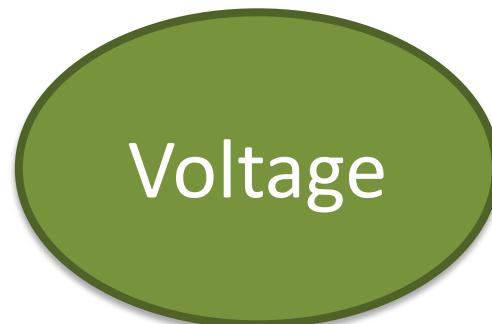
Anode and **cathode** are conventionally named following the **discharge direction**.

Figures of merit – criteria for improved LIBs

$$\text{Capacity} \times \text{Voltage} = \text{Energy Density}$$



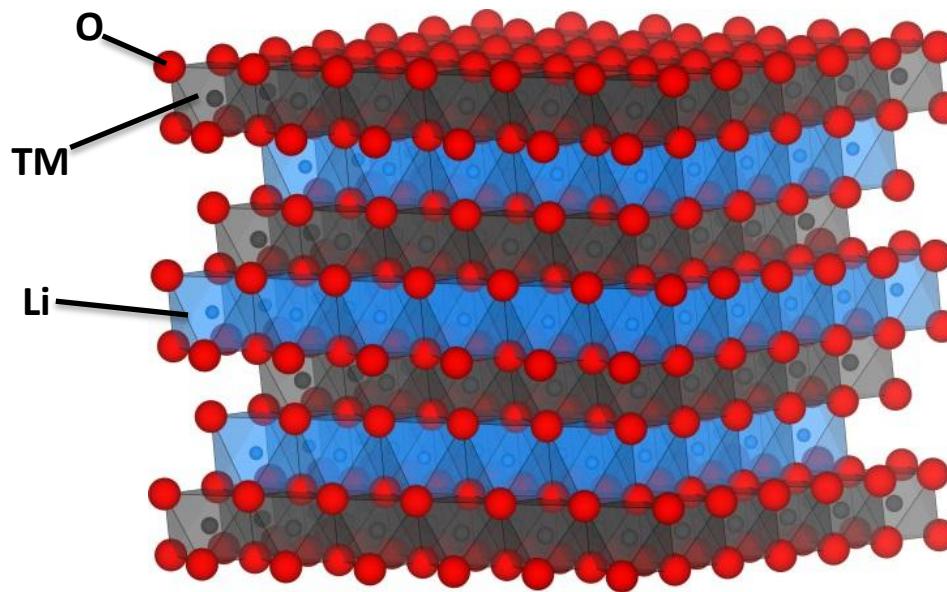
Amount of electrons (= Li) per mass or volume that can utilized



Potential difference between electrodes.

Cathode material (positive electrode) is current bottleneck for capacity & voltage.

Cathode research has focused on ordered TM oxides



O₃-type layered LiCoO_2 -structure

Close-packed O framework

Alternating Li and TM layers

High density

LCO (Co)

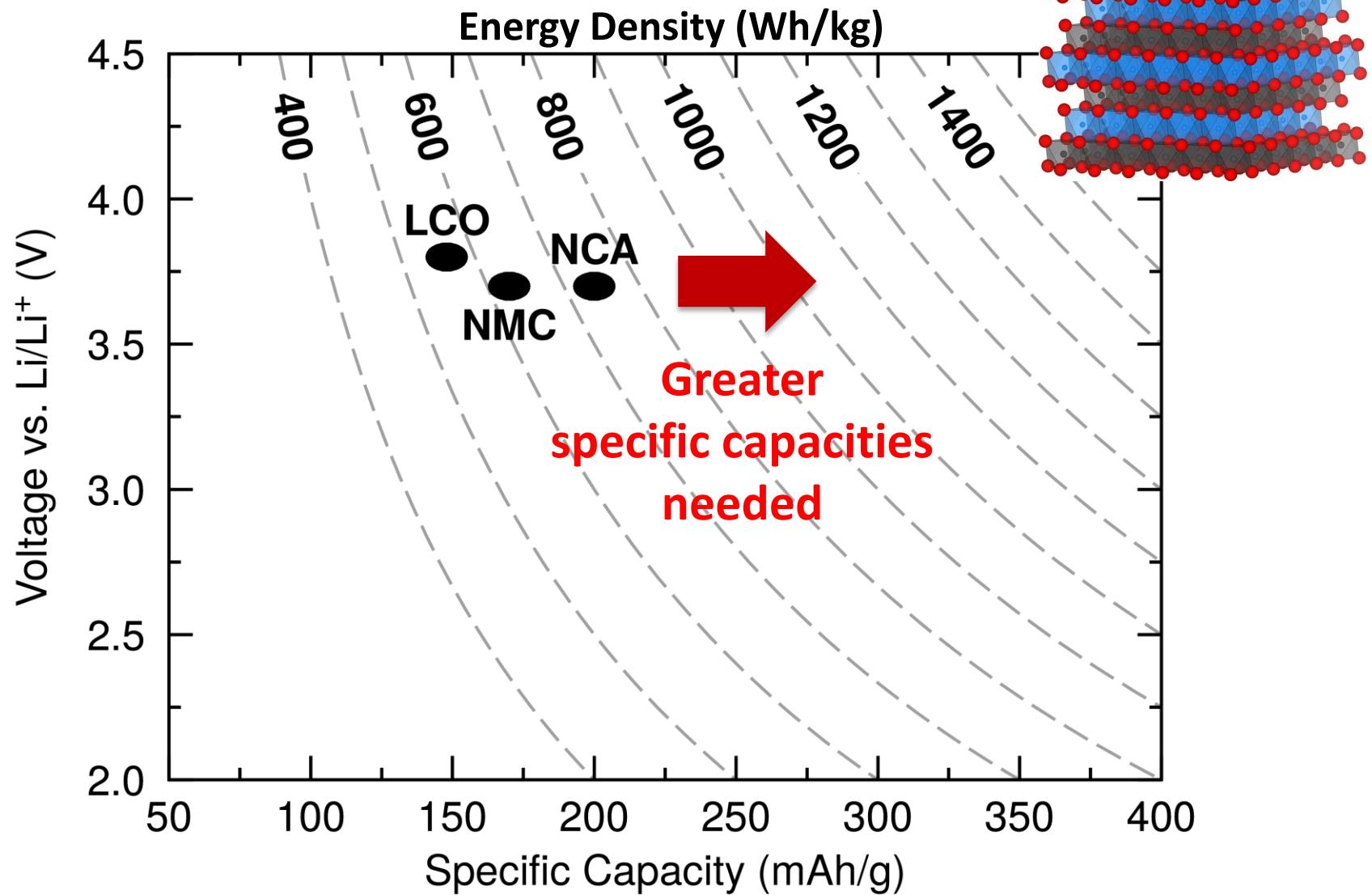
NCA (Ni, Co, Al)

NCM (Ni, Co, Mn)

Limitations

- Limited chemistry (Co, Ni, Mn, Al)
- Not entire Li content usable
- Limited capacity: 140-200 mAh/g

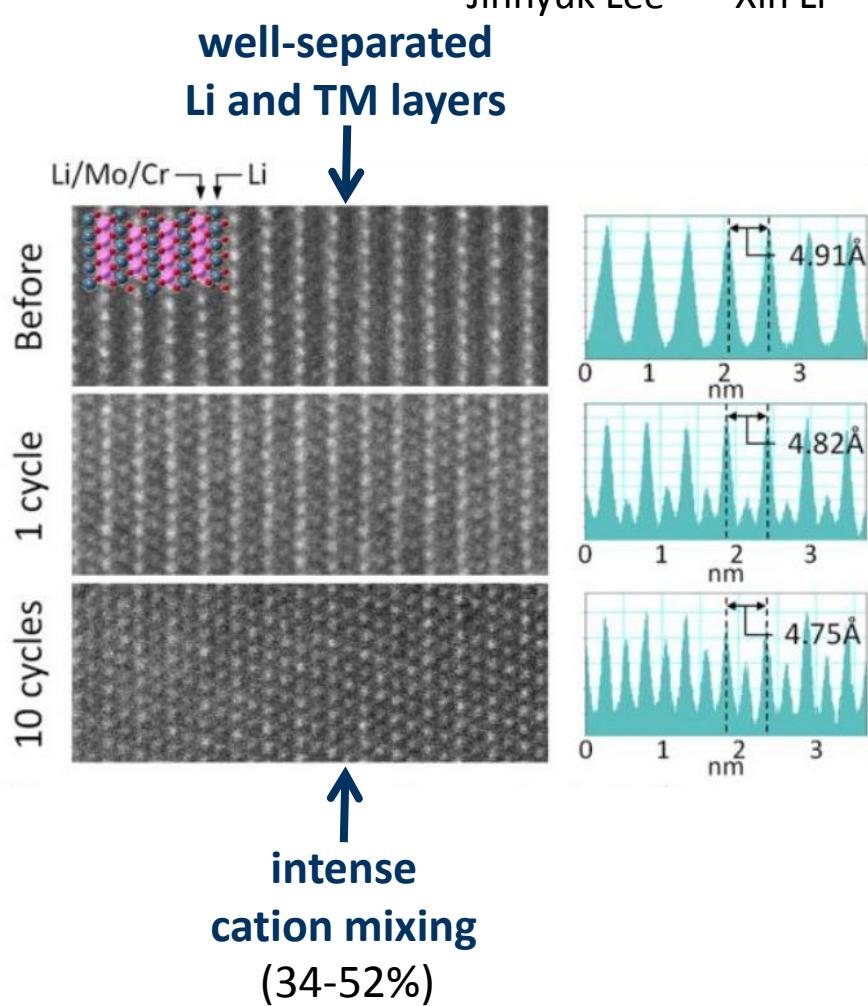
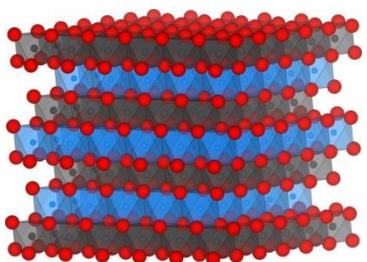
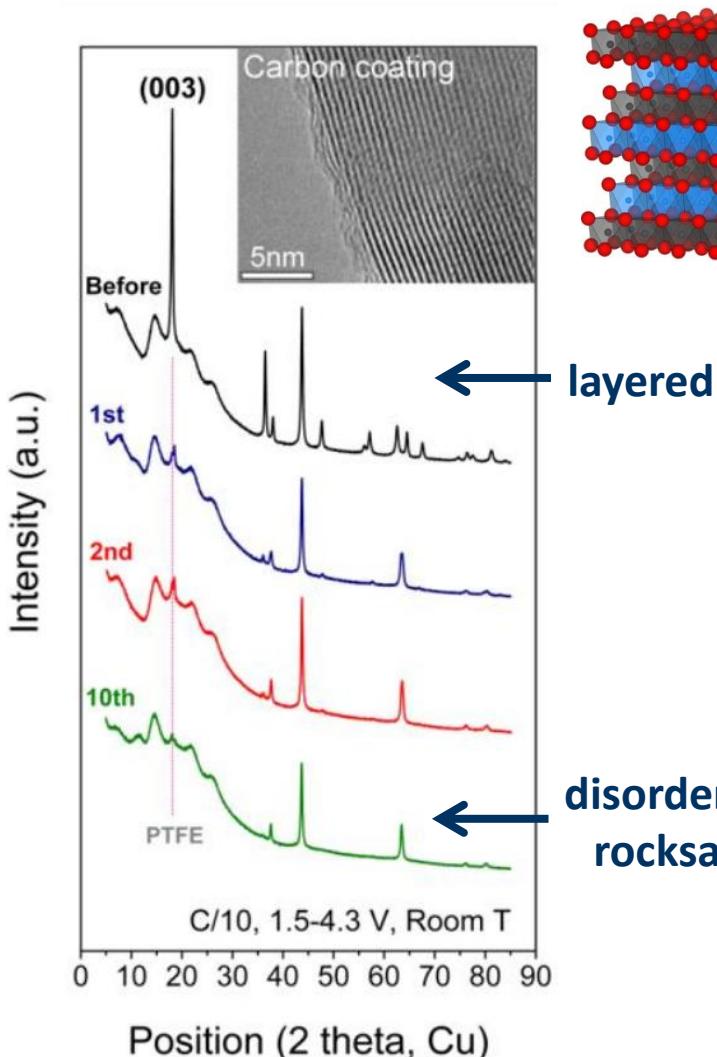
Energy densities of layered cathodes



Data from: Nitta et al., *Materials Today* **18** (2015) 252-264.

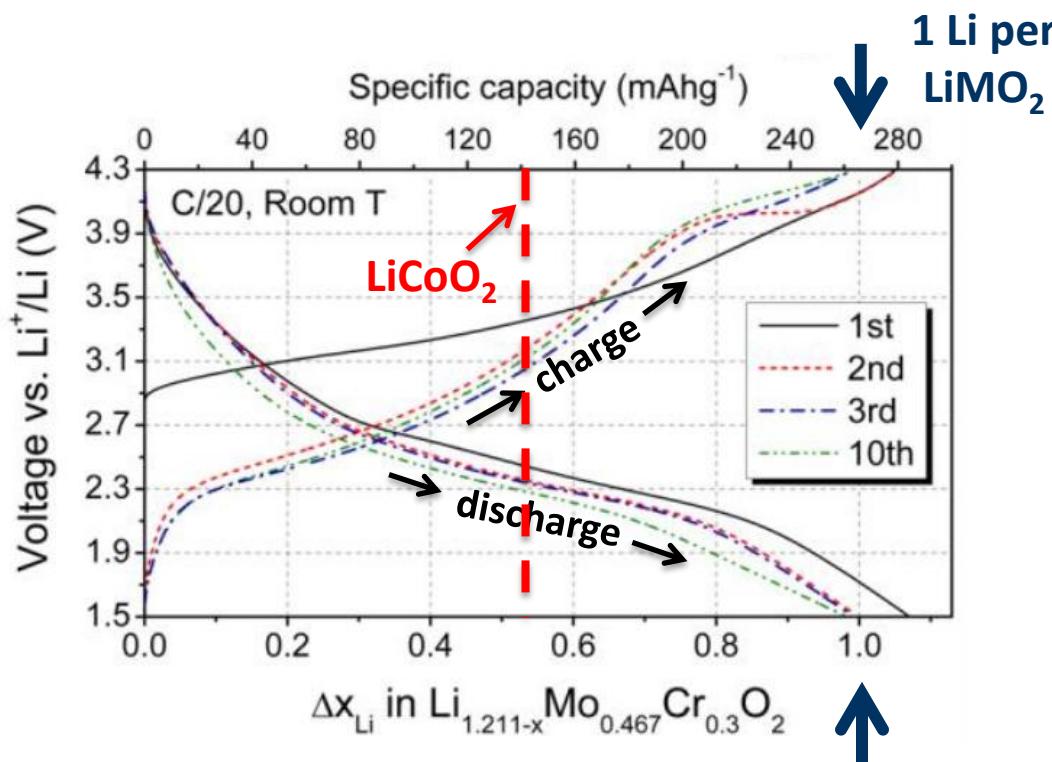
Cation-Disordered Cathode Materials for Li-Ion Batteries

Cation-disordered $\text{Li}_{1.211}\text{Mo}_{0.467}\text{Cr}_{0.3}\text{O}_2$ (LMCO)



J. Lee, A. Urban, X. Li, D. Su, G. Hautier, G. Ceder, *Science* **343** (2014) 519-522.

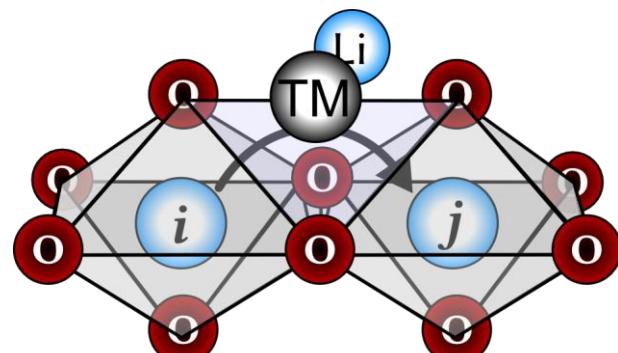
Cation-disordered LMCO has a remarkable capacity



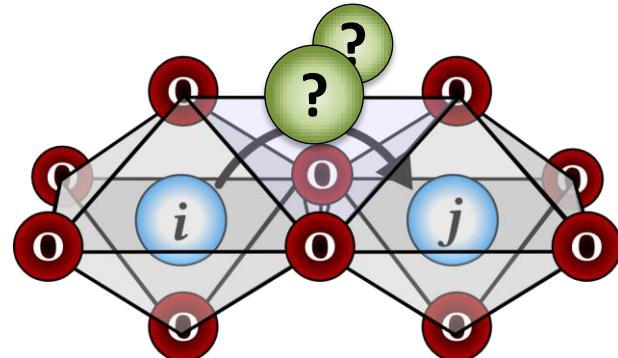
~1 Li atom per LiMO_2 formula unit can be reversibly cycled

J. Lee, A. Urban, X. Li, D. Su, G. Hautier, G. Ceder, *Science* **343** (2014) 519-522.

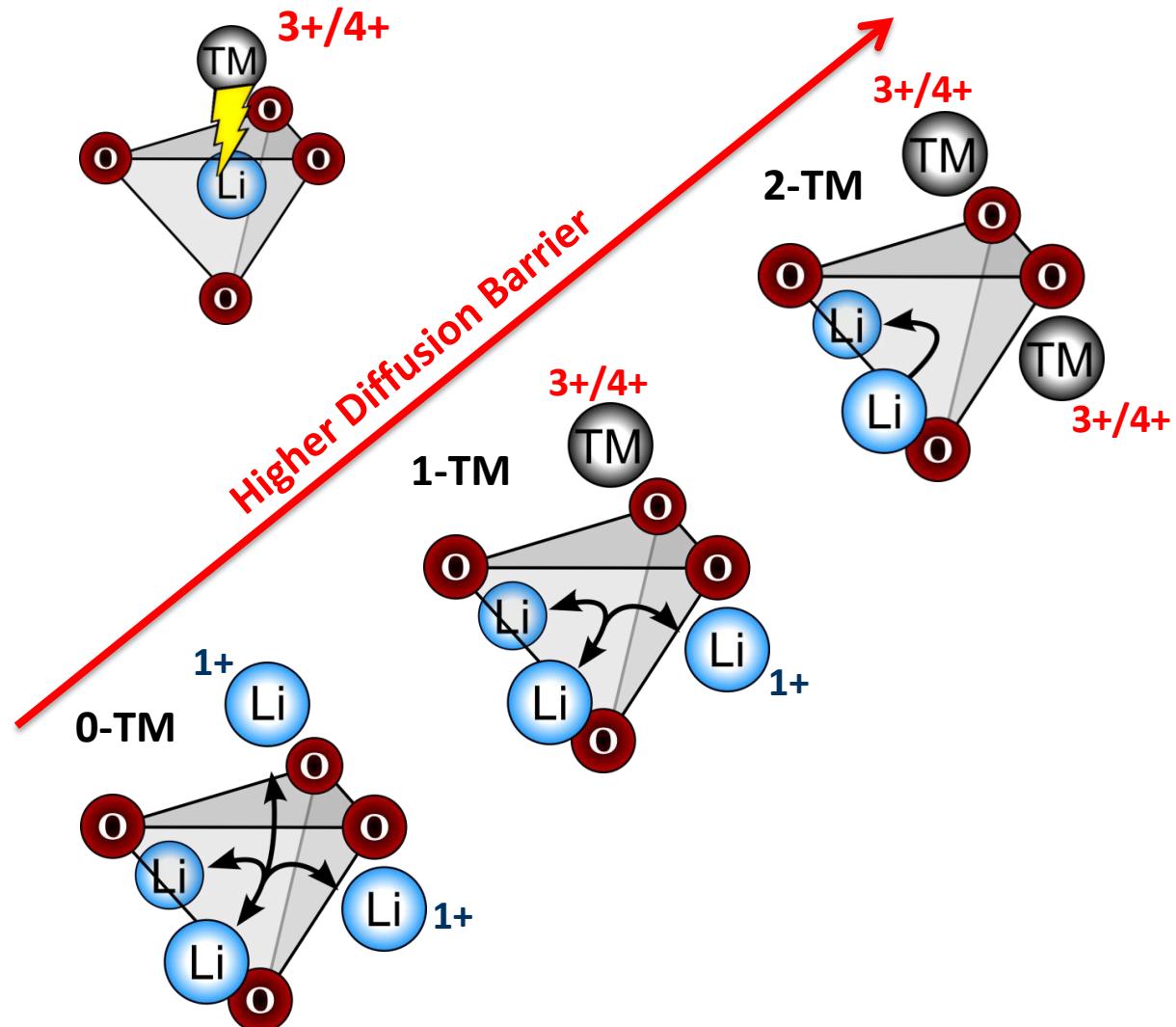
Cation-disorder creates fast o-TM diffusion channels



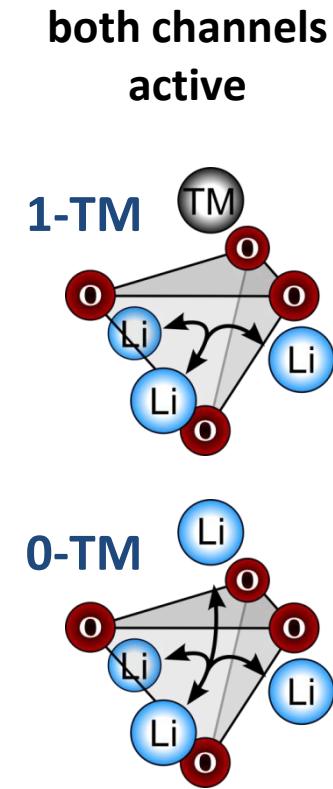
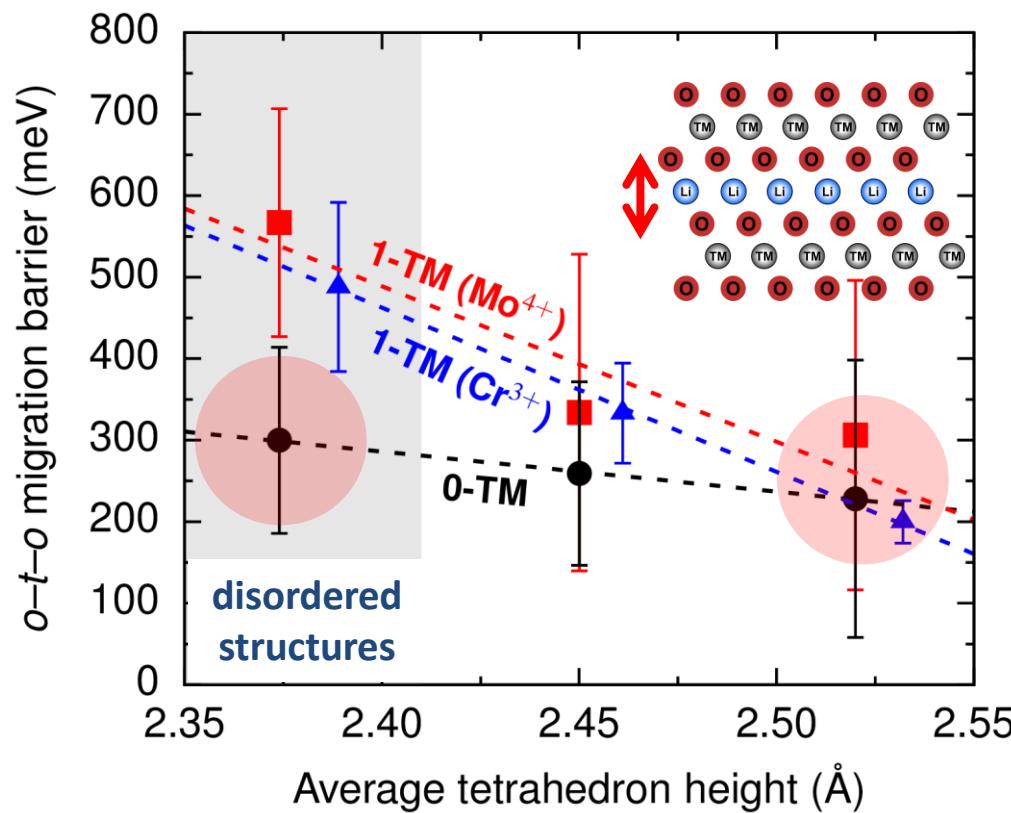
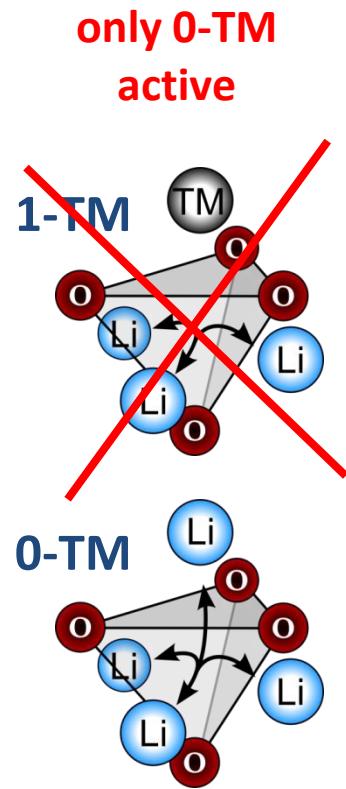
Layered



Cation disordered



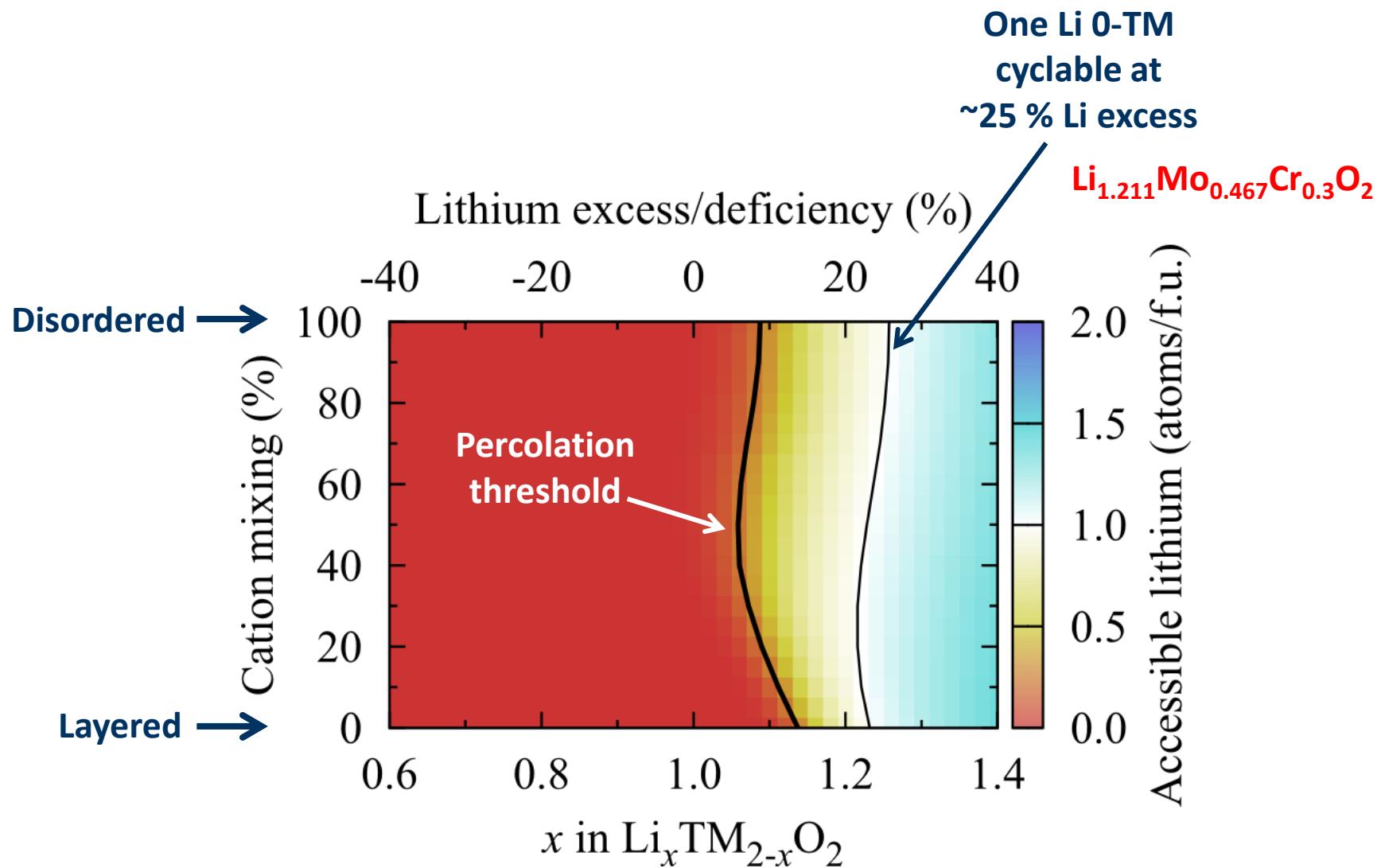
Only o-TM channels are active when disordered



Distribution of diffusion barriers calculated with DFT (PBE) and NEB

J. Lee, A. Urban, X. Li, D. Su, G. Hautier, G. Ceder, *Science* **343** (2014) 519-522.

Around 10% Li excess enables o-TM percolation



A. Urban, J. Lee, and G. Ceder, *Adv. Energy Mater.* **4** (2014) 1400478.

Impact on Li-ion battery cathode research

1991: $\text{Li}_3\text{V}_2\text{O}_5 = \text{Li}_{1.2}\text{V}_{0.8}\text{O}_2$

C. Delmas, S. Brèthes and M. Ménétrier $\omega\text{-Li}_x\text{V}_2\text{O}_5$, *J. Power Sources* **34** (1991) 113-118.

1998: LiMO_2 (**M**=Ti, Mn, Fe, Co, Ni) by mechanochemical synthesis (ball-milling)

M. Obrovac, O. Mao, and J. Dahn, *Solid State Ionics* **112** (1998) 9-19.

2014: $\text{Li}_{1.211}\text{Mo}_{0.467}\text{Cr}_{0.3}\text{O}_2$

J. Lee, A. Urban, X. Li, D. Su, G. Hautier, and G. Ceder, *Science* **343** (2014) 519-522.

2015: $\text{Li}_2\text{VO}_2\text{F} = \text{Li}_{1.333}\text{V}_{0.666}\text{O}_{1.333}\text{F}_{0.666}$

R. Chen, S. Ren, M. Knapp, D. Wang, R. Witter, M. Fichtner, and H. Hahn, *Adv. Energy Mater.* **5** (2015) 1401814.

2015: $\text{Li}_{1.3}\text{Nb}_x\text{M}_{0.7-x}\text{O}_2$ (**M** = Mn, Fe, Co, Ni)

N. Yabuuchi, M. Takeuchi, M. Nakayama, H. Shiiba, M. Ogawa, K. Nakayama, T. Ohta, D. Endo, T. Ozaki, T. Inamasu, K. Sato, and S. Komaba, *Proc. Natl. Acad. Sci. USA* **112** (2015) 7650–7655.

2015: $\text{Li}_{1.25}\text{Nb}_{0.25}\text{Mn}_{0.5}\text{O}_2$

R. Wang, X. Li, L. Liu, J. Lee, D.-H. Seo, S.-H. Bo, A. Urban, G. Ceder, *Electrochim. Commun.* **60** (2015) 70–73.

2015: $\text{Li}_{1.2}\text{Ni}_{0.333}\text{Ti}_{0.333}\text{Mo}_{0.133}\text{O}_2$

J. Lee, D.-H. Seo, M. Balasubramanian, N. Twu, X. Li and G. Ceder, *Energy Environ. Sci.* **8** (2015) 3255–3265.

2015: $\text{Li}_{1+x}\text{Ti}_{2x}\text{Fe}_{1-3x}\text{O}_2$

S. L. Glazier, J. Li, J. Zhou, T. Bond and J. R. Dahn, *Chem. Mater.* **27** (2015) 7751–7756.

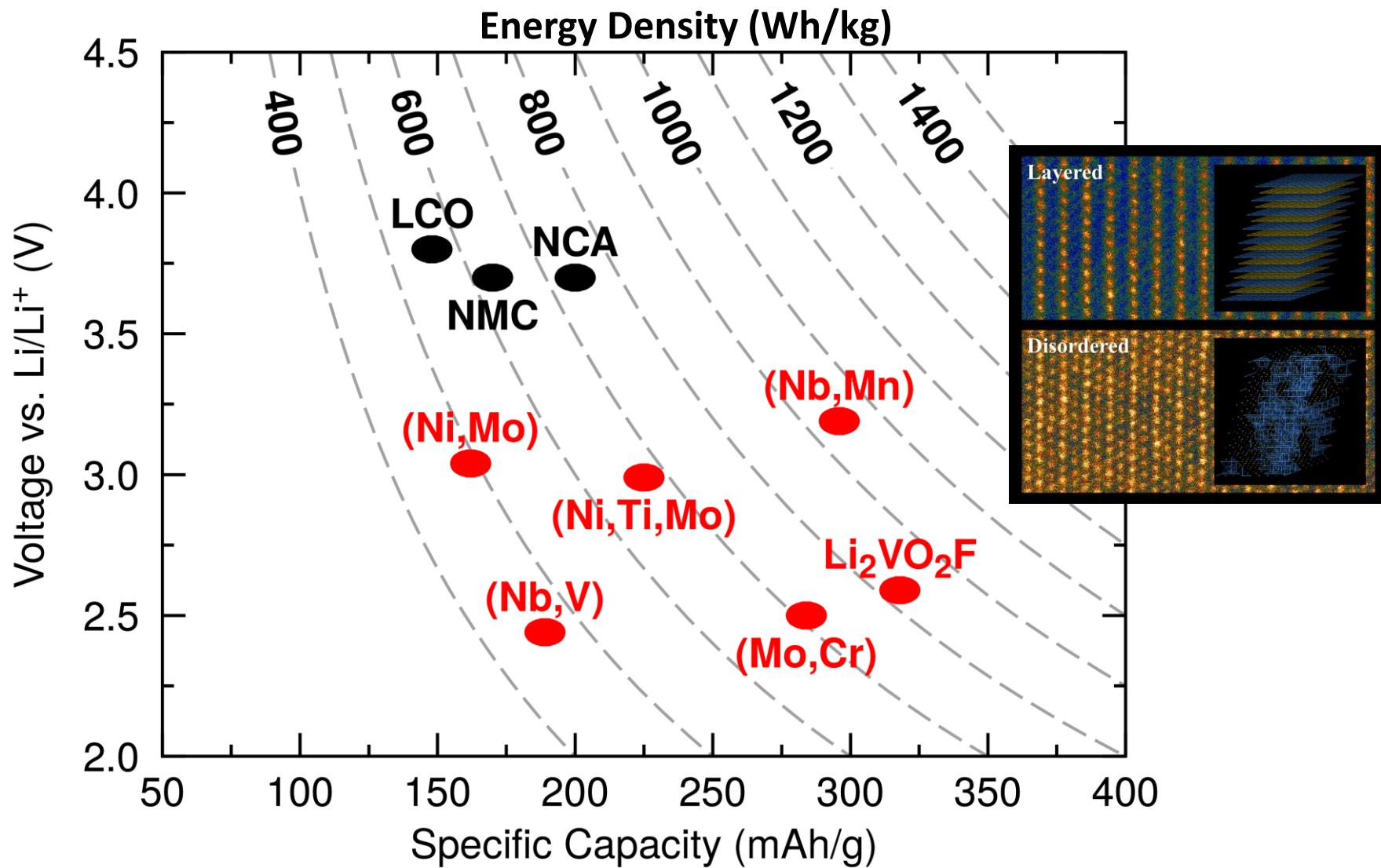
2016: $\text{Li}_{1.333}\text{Ni}_{0.333}\text{Mo}_{0.333}\text{O}_2$

N. Yabuuchi, Y. Tahara, S. Komaba, S. Kitada and Y. Kajiya, *Chem. Mater.* **28** (2016) 416-419.

2016: $\text{Li}_{1.3}\text{Nb}_{0.3}\text{V}_{0.4}\text{O}_2$

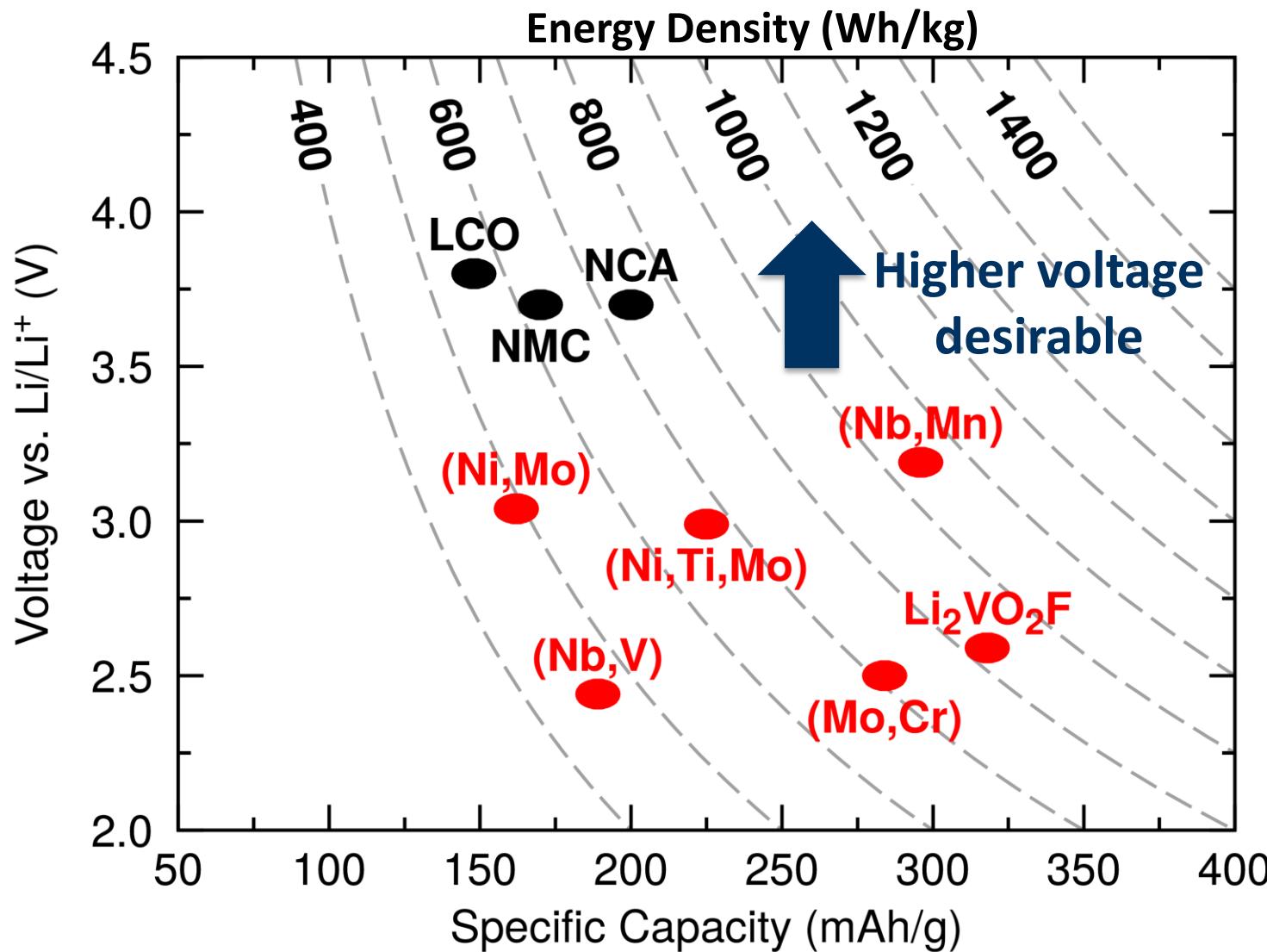
N. Yabuuchi, M. Takeuchi, S. Komaba, S. Ichikawa, T. Ozaki, and T. Inamasu, *Chem. Commun.* **52** (2016) 2051-2054.

The new materials have high energy densities



LCO, NMC, NCA data from: Nitta et al., *Materials Today* **18** (2015) 252-264.

Can disordered materials achieve high voltages?

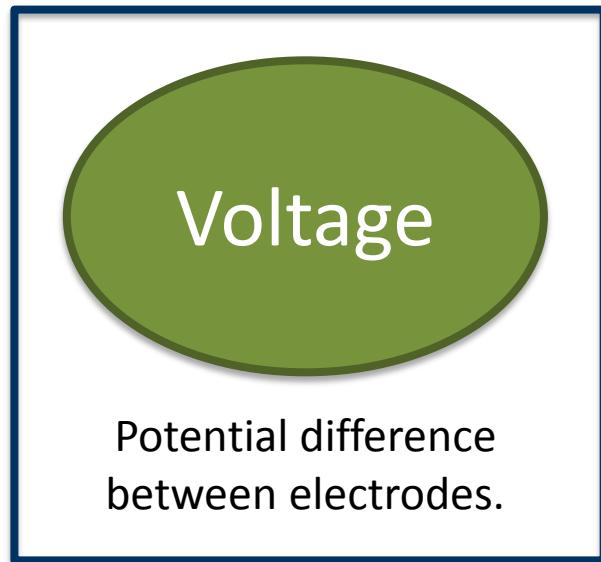


LCO, NMC, NCA data from: Nitta et al., *Materials Today* **18** (2015) 252-264.

Figures of merit – criteria for improved LIBs

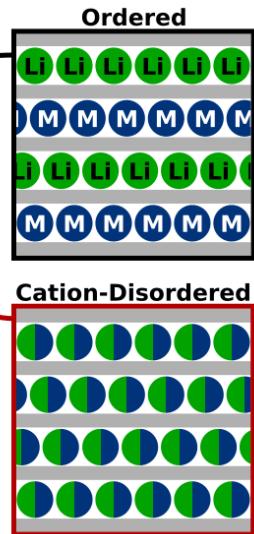
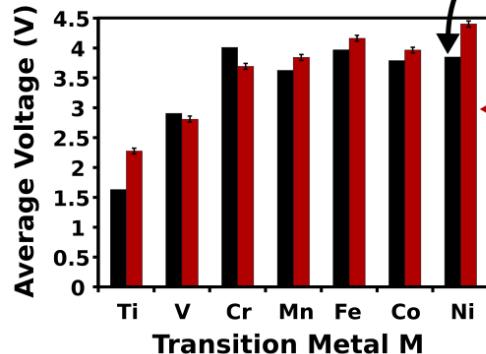


Amount of electrons (= Li) per mass
or volume that can utilized

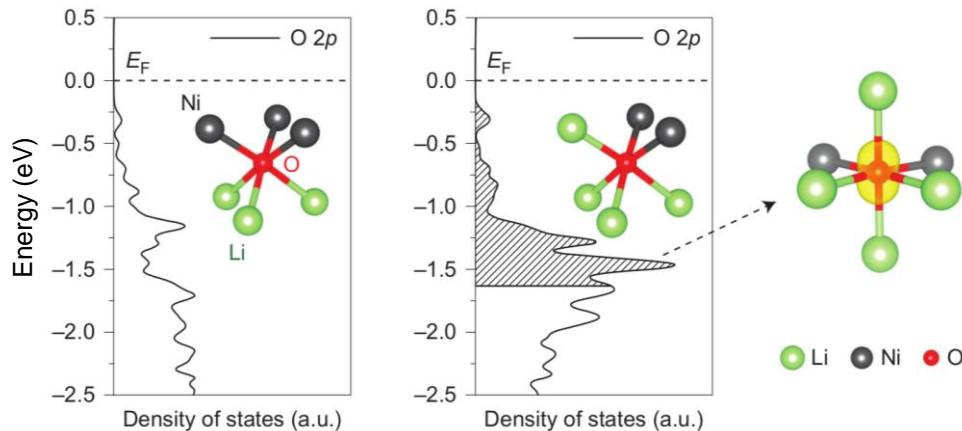


Potential difference
between electrodes.

Effect of disorder on redox & voltage



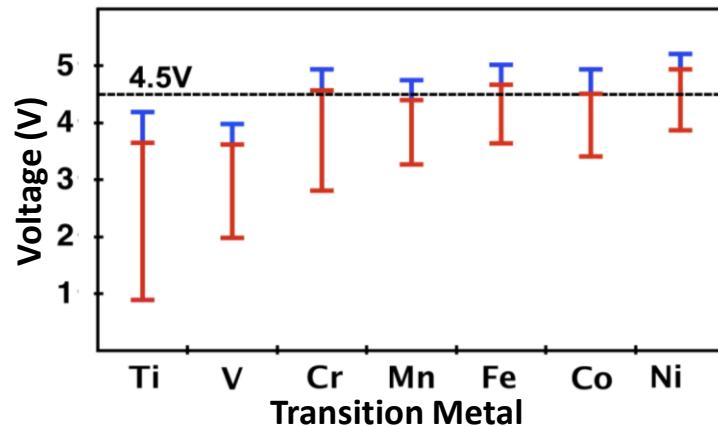
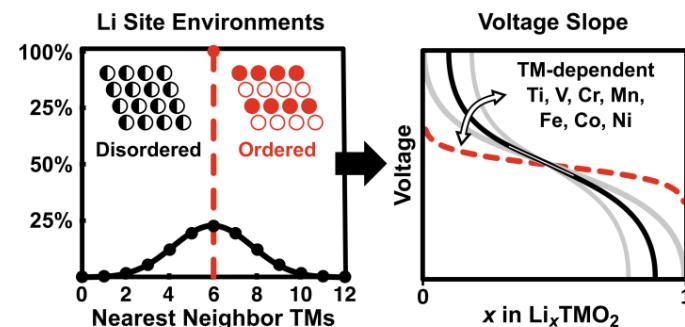
A. Abdellahi†, A. Urbant, S. Dacek, and G. Ceder,
Chem. Mater. **28** (2016) 5659-3665.



D.-H. Seo, J. Lee, A. Urban, R. Malik, S. Kang,
and G. Ceder, *Nat. Chem.* **8** (2016) 692-697



Aziz Abdellahi Dong-Hwa Seo Jinyuk Lee



A. Abdellahi, A. Urban, S. Dacek, and G. Ceder,
Chem. Mater. **28** (2016) 5373-5383.

Current understanding of cation disorder

1. Cation order does (almost) not matter for capacity

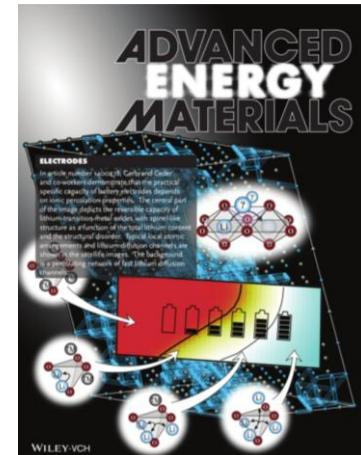
- Cation mixing does not affect practical capacity for compositions with more than **15% Li excess**

2. Cation disorder may increase structural stability

- Increased structural stability (lattice parameters)

3. Disorder affects the voltage

- Average voltage & voltage profile (slope)
- Redox mechanism, oxygen redox → **Dong-Hwa Seo**



A. Urban, J. Lee, and G. Ceder, *Adv. Energy Mater.* **4** (2014) 1400478.

J. Lee, A. Urban, X. Li, D. Su, G. Hautier, G. Ceder, *Science* **343** (2014) 519-522.

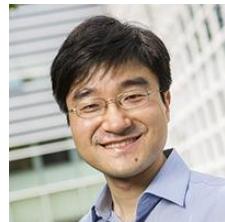
Acknowledgments



Dong-Hwa Seo



Jinhyuk Lee



Xin Li



Aziz Abdellahi

(now Harvard U) (now at A123)



Gerd Ceder



BOSCH

