US Department of Energy (DOE) Office of Electricity Delivery and Energy Reliability
in collaboration with the Pacific Northwest National Laboratory

Prussian Blue Materials for Na-ion Batteries

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Why Na-ion batteries?

Sources

G

Cost

$

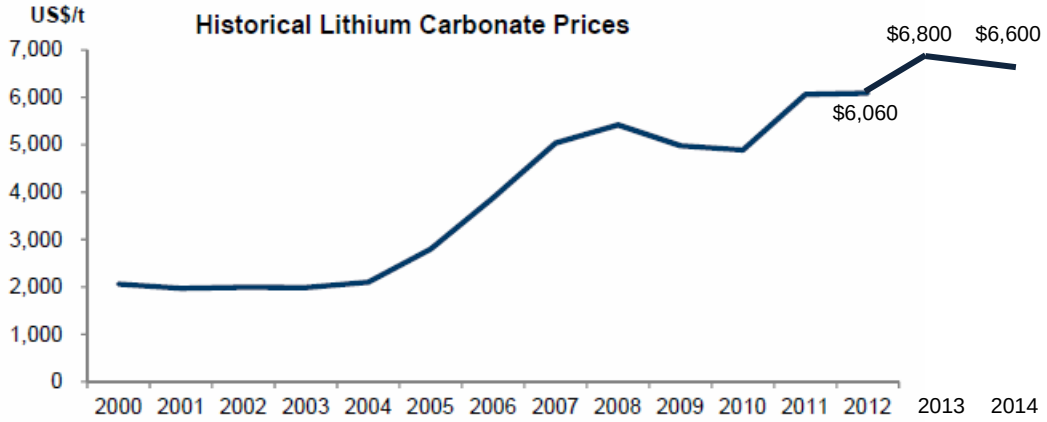
Table 1. Sodium versus Lithium characteristics.

Lithium	Sodium	Category
0.76	1.06	Cation radius (Å)
6.9 g mol^{-1}	23 g mol^{-1}	Atomic weight
0	0.3 V	E^{o} (vs. Li/Li^{+})
$5000/ton	$150/ton	Cost, carbonates
3829	1165	Capacity (mAh g^{-1}), metal
Octahedral and tetrahedral	Octahedral and prismatic	Coordination preference

Christopher S. Johnson *et al.*, ***Adv. Funct. Mater.*** 23, 947 (2013).

Energy

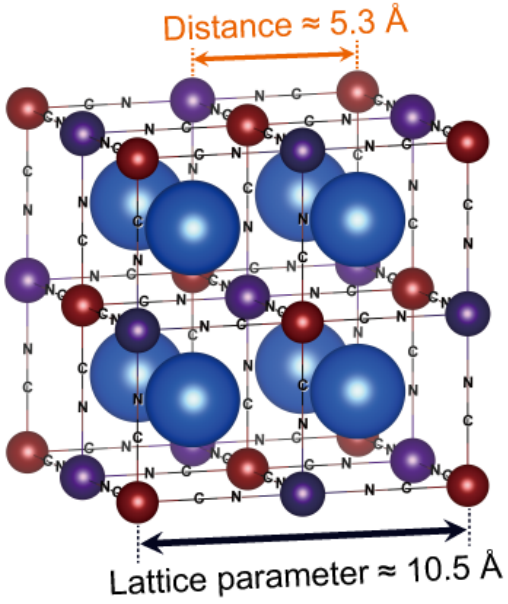
Exhibit 8: Lithium Carbonate Prices



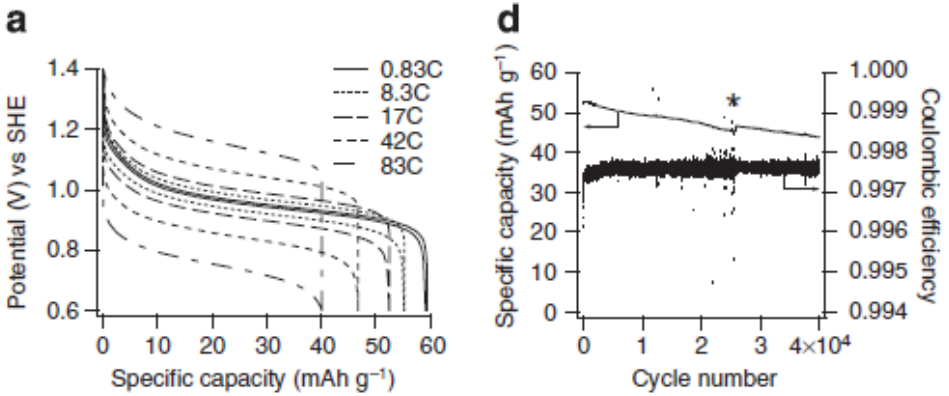
Ref) Roskill and signumBox and U.S. Geological Survey, Mineral Commodity Summaries, January 2015

What is Prussian Blue open-framework?

- **Prussian Blue open framework structure**
  - High energy efficiency and long cycle life



The performance for Na ion battery in an aqueous electrolyte



- **Aqueous battery (water-based electrolyte)**
  - High ionic conductivity, non-flammable, high solubility, and cheap
  - An aqu' battery has attracted wide attention as a **grid scale energy storage**.

C. Wessells, Y. Cui *et al.*, *Nat. Commun.* **2**, 550, (2011).

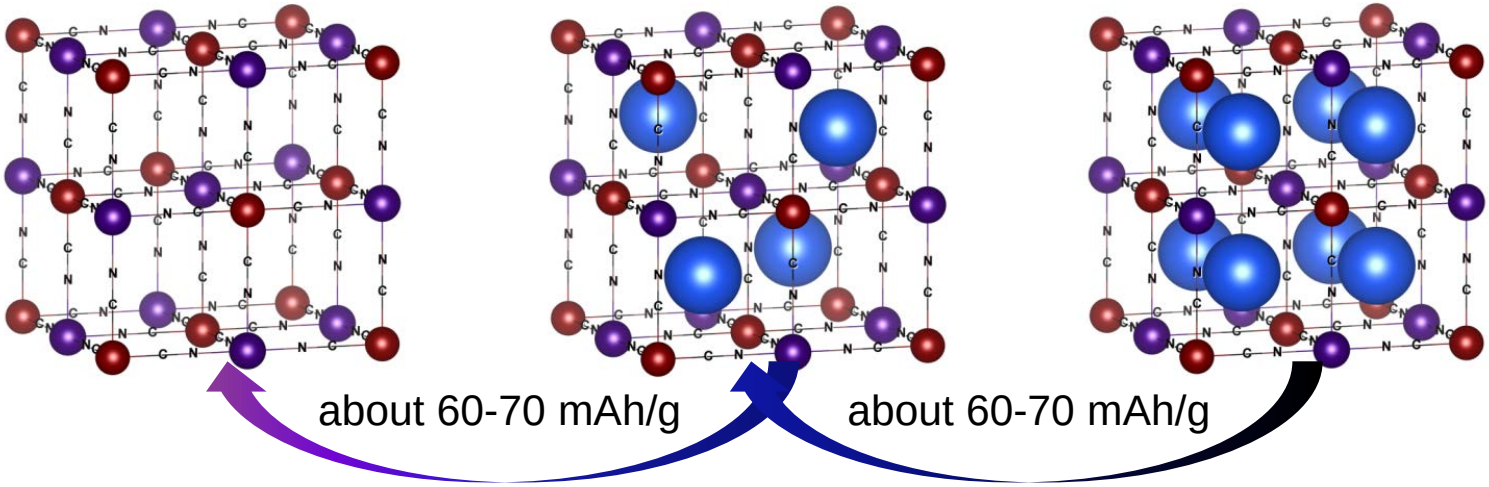
Capacity due to the reaction of TM ions

- General electrochemical reactions

$$Capacity = \frac{Number\ of\ ions \quad (Sites\ to\ insert)}{Molecular\ weight \quad (Weight\ of\ a\ cage)}$$

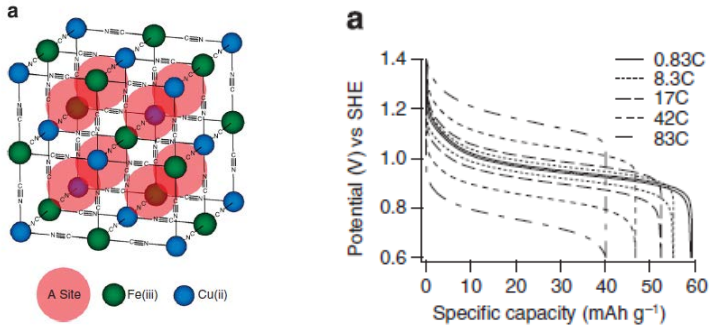
Reaction of N-coordinated metal ion

Reaction of C-coordinated metal ion



Energy storage applications

Cathode

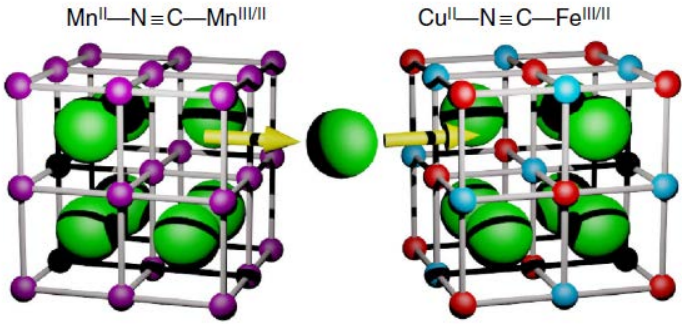


C. Wessells, Y. Cui *et al.*, *Nat. Commun.* **2**, 550 (2011).

C. Wessells, Y. Cui *et al.*, *Nano Lett.*, **11**, 5421 (2011).

C. Wessells, Y. Cui *et al.*, *ACS Nano*, **6**, 1688 (2012).

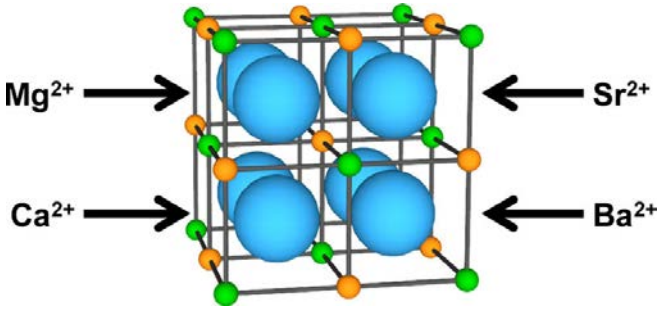
Anode



M. Pasta, Y. Cui *et al.*, *Nat. Commun.* **3**, 1149 (2012).

M. Pasta, Y. Cui *et al.*, *Nat. Commun.* **5**, 3007 (2014).

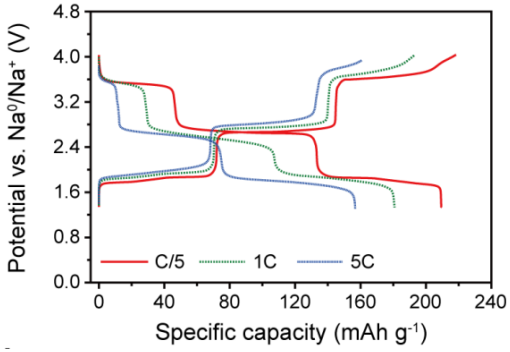
Divalent ions



R. Wang, Y. Cui *et al.*, *Nano Lett.*, **13**, 5748 (2013).

R. Wang, Y. Cui *et al.*, *Adv. Energy Mater.* **5** 1401869 (2015).

In organic electrolyte



H.-W. Lee, Y. Cui *et al.*, *Nat. Commun.* **5**, 5280 (2014).

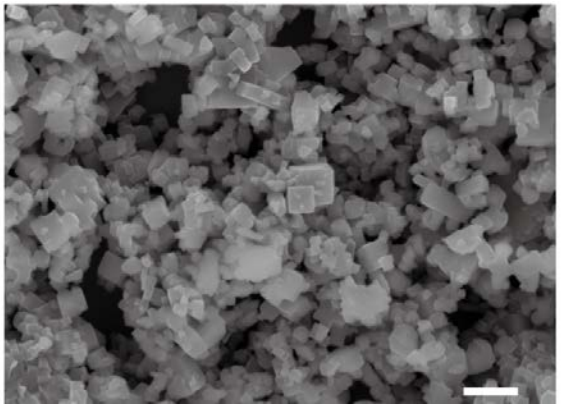
H.-W. Lee, Y. Cui *et al.*, *Faraday Discuss.* **176**, 69-81 (2014).

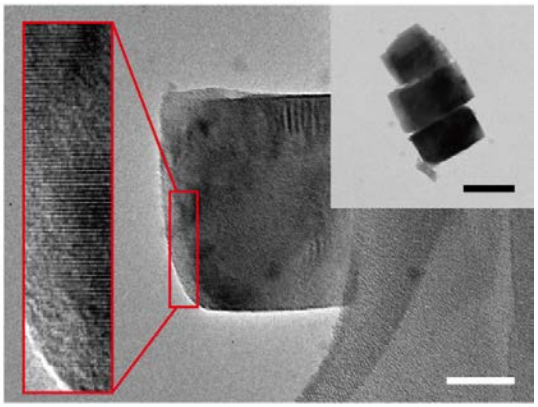
A Manganese based Prussian Blue analogue

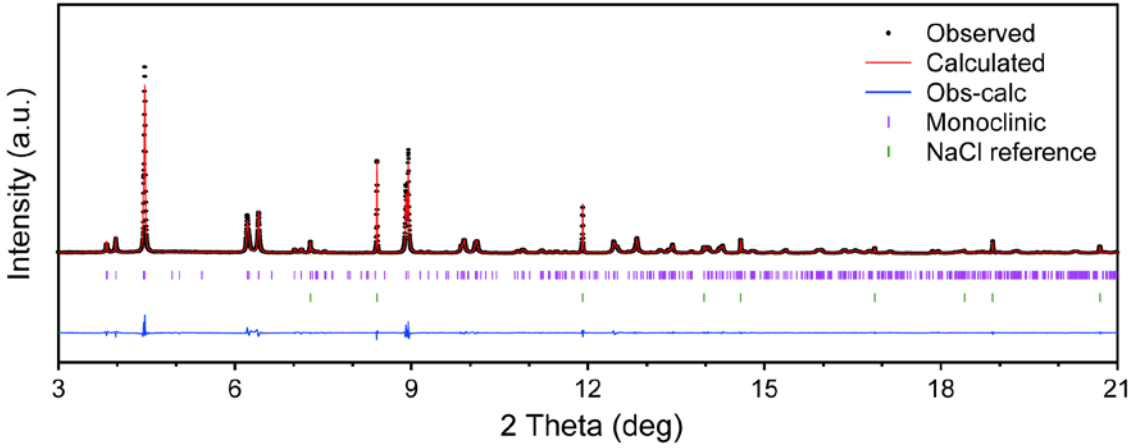
- **Merits of Manganese (Mn)**
  - **Abundant element**, which makes it suitable for low-cost battery applications
  - Several **electrochemically accessible valence states** that increase the number of possible redox reactions in the structure; this allows the structure to accommodate more cations, which improves the specific capacity.
- **Easy synthesis**

$Na_2Mn^{II}[Mn^{II}(CN)_6]$, for high capacity cathode

- The initial state of the sample is $Na_2Mn^{II}[Mn^{II}(CN)_6]$
  - ICP data: $\mathbf{Na_{1.96}Mn[Mn(CN)_6]_{0.99}\cdot\square_{0.01}}$, where □ represents a $[Mn(CN)_6]$ vacancy.
- Low vacancy, monoclinic crystal phase

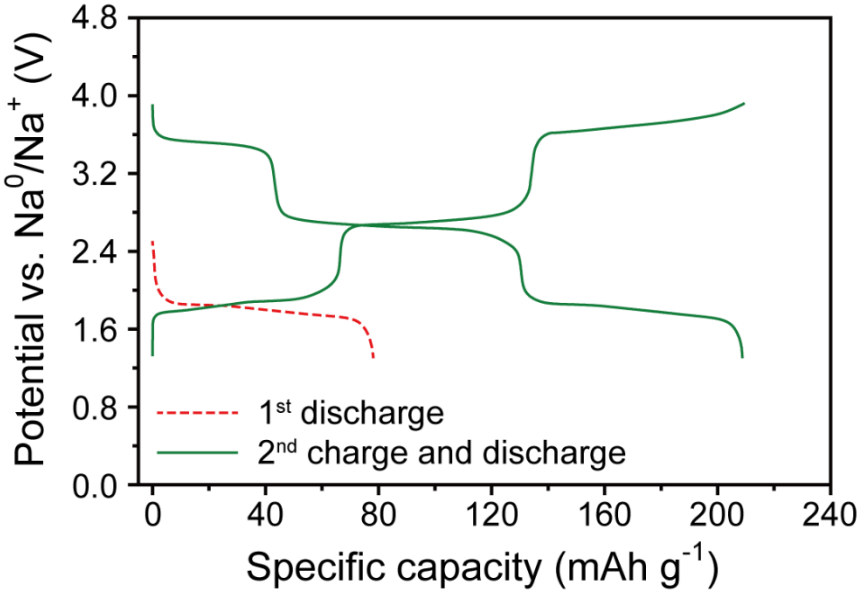


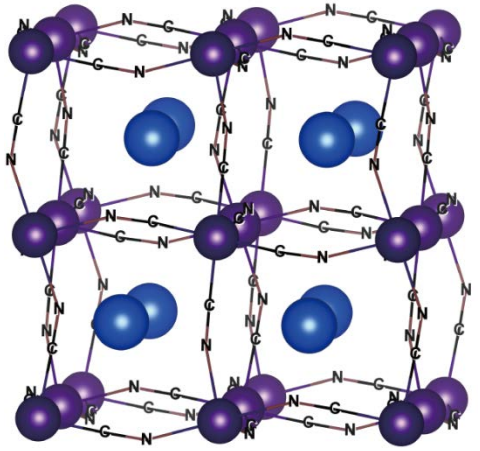




$Na_2Mn^{II}[Mn^{II}(CN)_6]$ (MnHCMn)

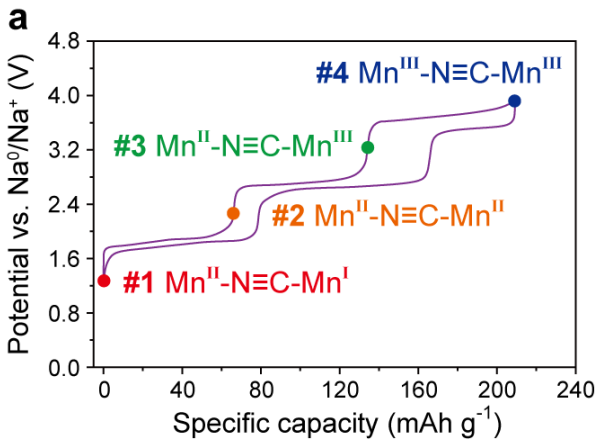
- **Electrochemical performance in Na-ion battery**
  - OCV is about 2.4 V vs. Na/Na^+
  - Three distinct plateaus were observed.

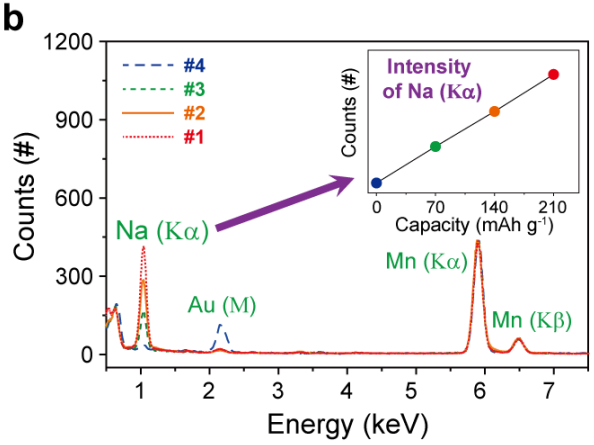


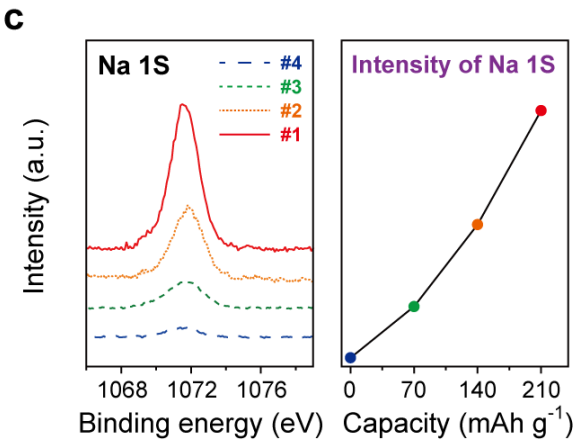


Chemical analysis

- **Chemical analysis at the end points of each Na^+ ion insertion reaction plateau**
  - EDS and XPS of Na data confirmed the amount of Na increases at every each step.







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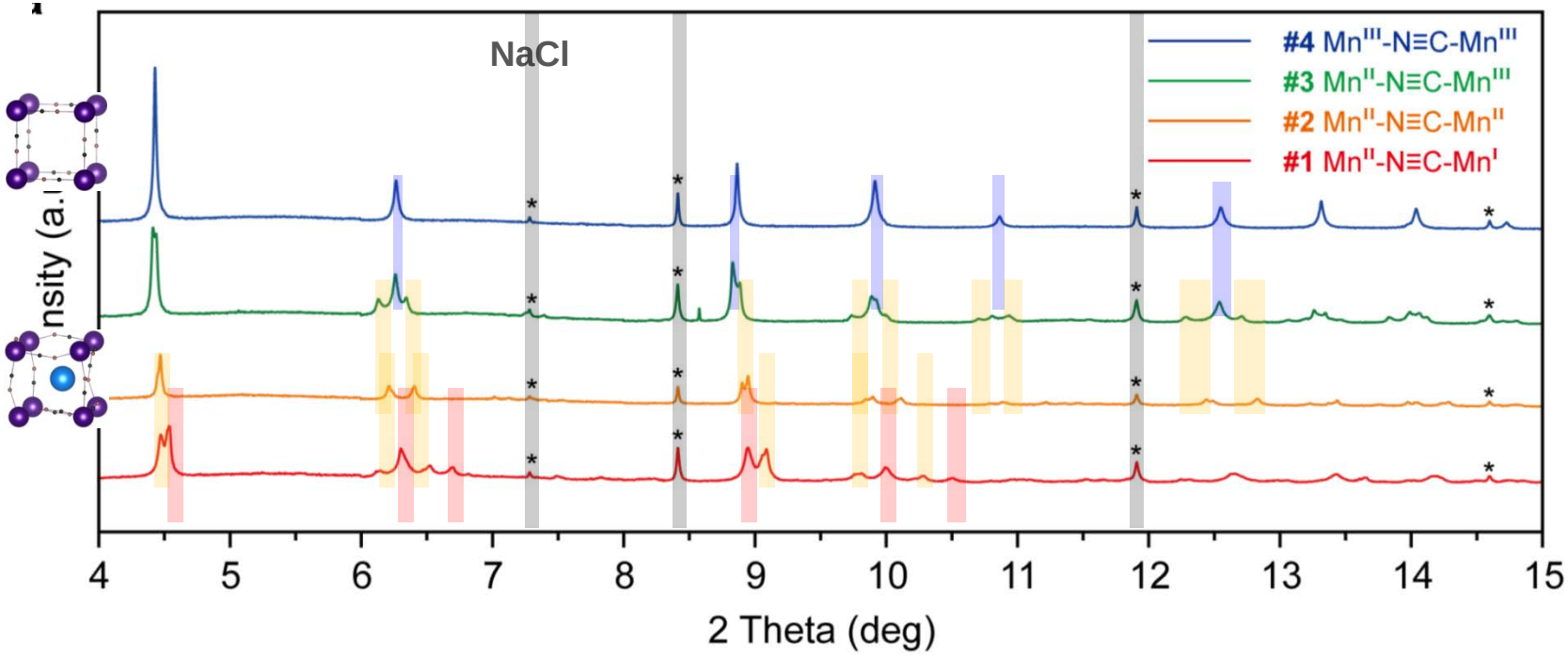
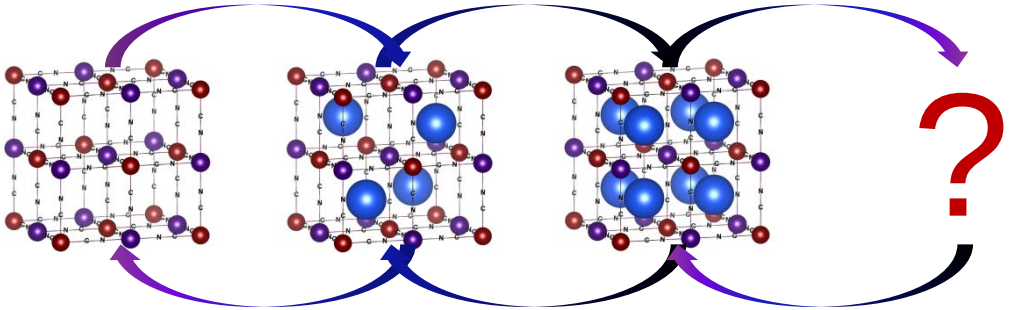
$$Na_3Mn^{II}[Mn^{I}(CN)_6] \rightleftharpoons Na_2Mn^{II}[Mn^{II}(CN)_6] \rightleftharpoons Na_1Mn^{II}[Mn^{III}(CN)_6] \rightleftharpoons Na_0Mn^{III}[Mn^{III}(CN)_6]$$

(Initial state)

Structural analysis

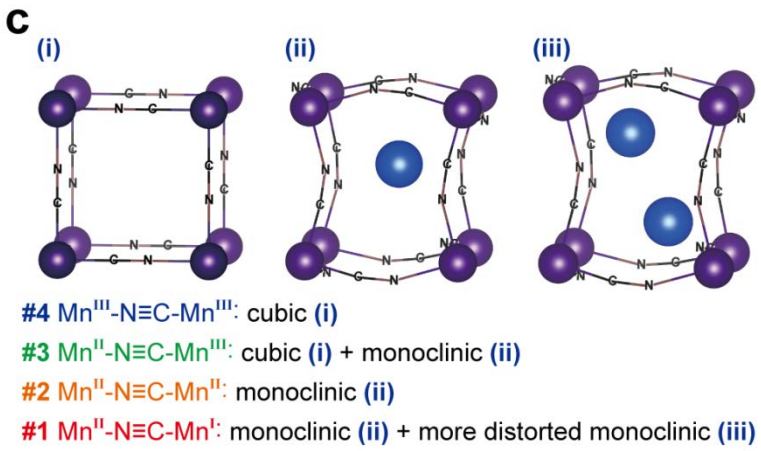
- **Structural analysis – *ex situ* XRD**

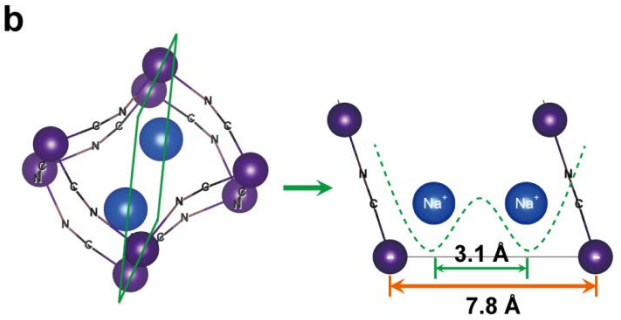


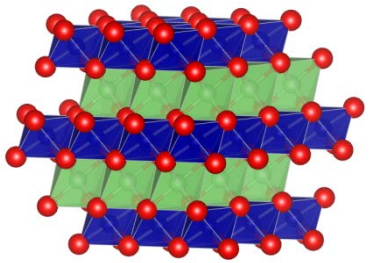


Two Na^+ ions within one subunit cell

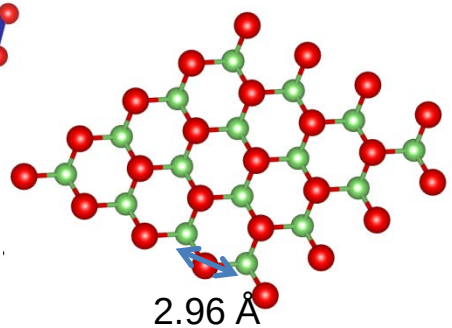
- Geometric consideration

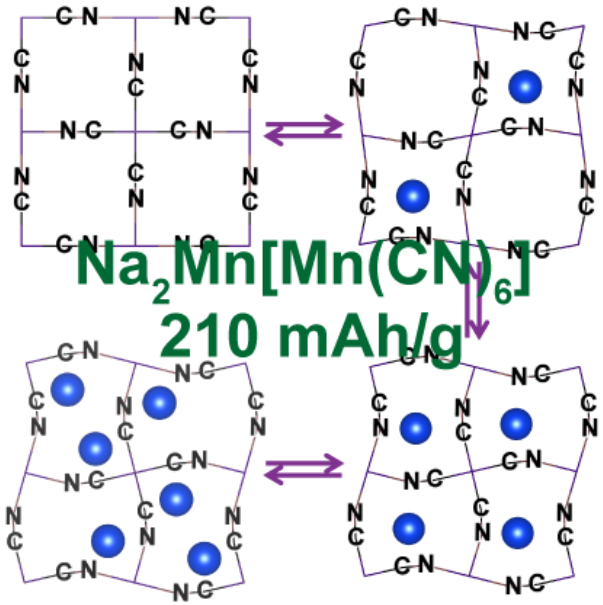






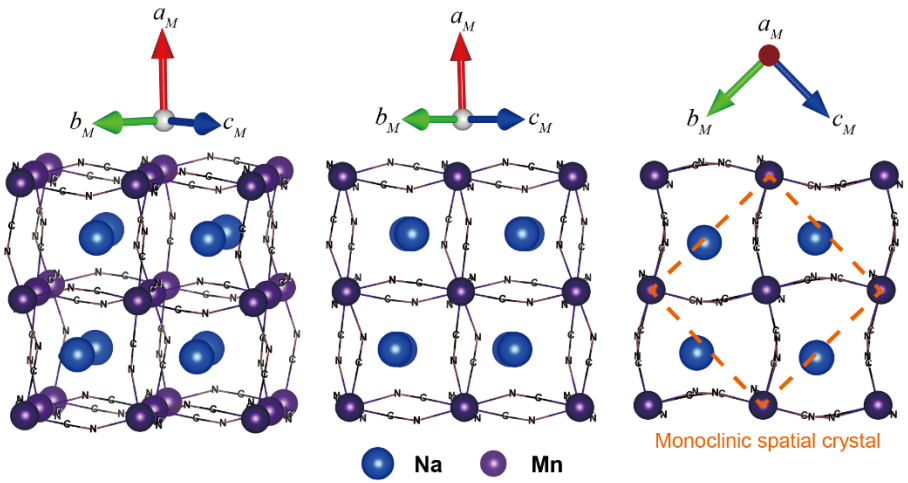
$Na_{2/3}[Fe_{1/2}Mn_{1/2}]O_2$ –Nat. Mater.
Rhombohedral structure (R-3m)
$a = b = 2.959$Å, $c = 16.522$Å,
$\alpha = \beta = \gamma = 90^o$





H.-W. Lee *et al.*, *Nat. Commun.* **5**, 5280, (2014).

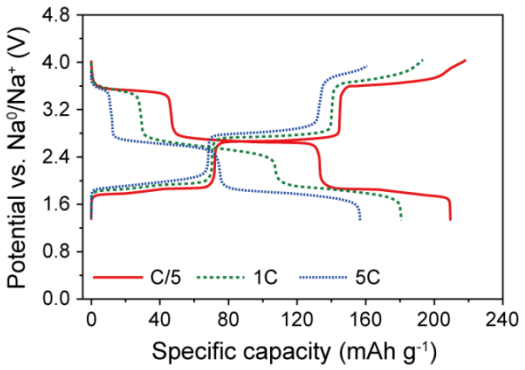
Volume expansion and shrinkage

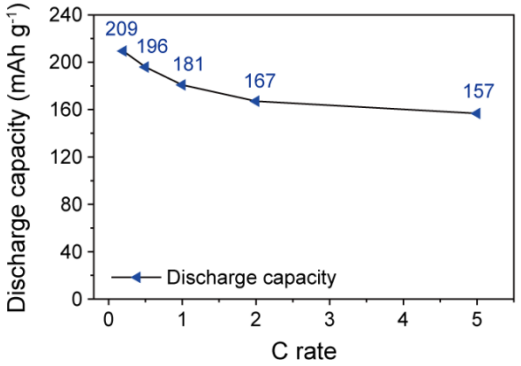


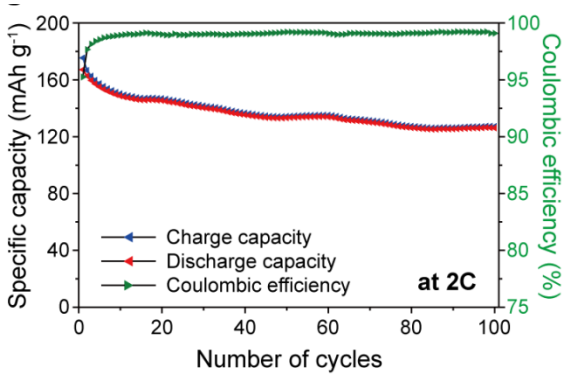
	Lattice parameter (Å)			Angle (°)			Difference (%)			Volume expansion (%)
	a	*b*	*c*	*α*	*β*	*γ*	*a*	*b*	*c*	*V*
#4 Mn^{III}-N≡C-Mn^{III}	10.706	10.706	10.706	90	90	90				
#3 Mn^{II}-N≡C-Mn^{III}	10.688	10.750	10.750	90	90	90	-0.17	0.41	0.41	0.65
#2 Mn^{II}-N≡C-Mn^{II}	10.658	10.616	10.616	90	92.43	90	-0.28	-1.25	-1.25	-2.75
#1 Mn^{II}-N≡C-Mn^{I}	10.459	10.905	10.905	90	108.84	90	-1.87	2.72	2.72	3.55

Battery performance of MnHCMn

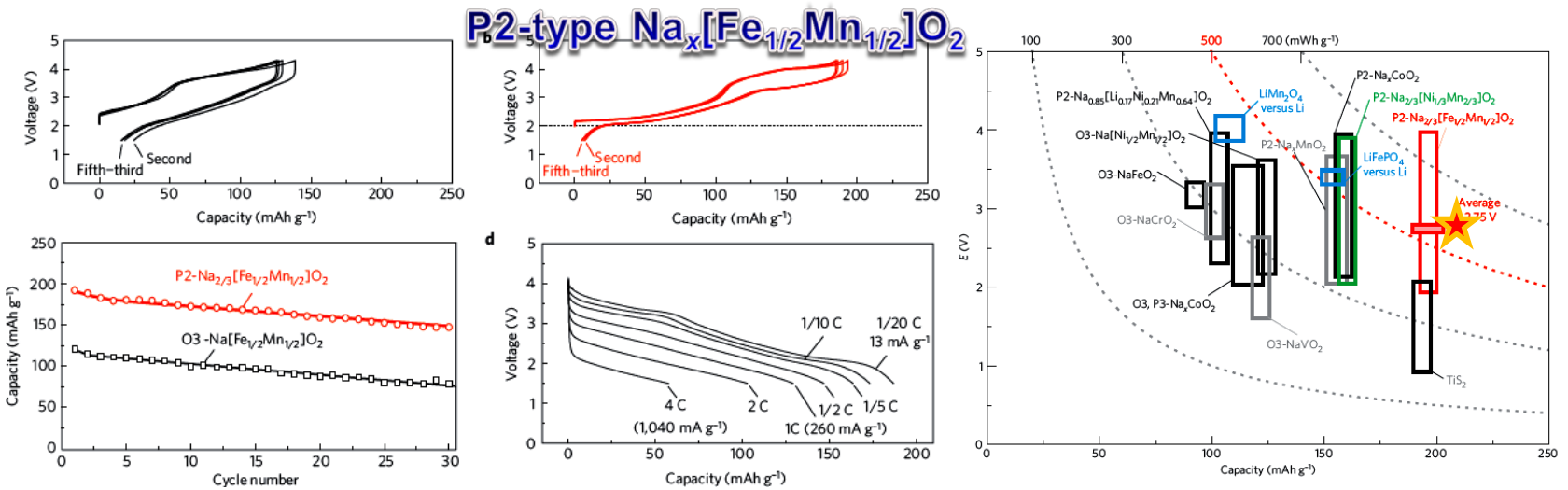
- **As a cathode material for Na-ion battery**







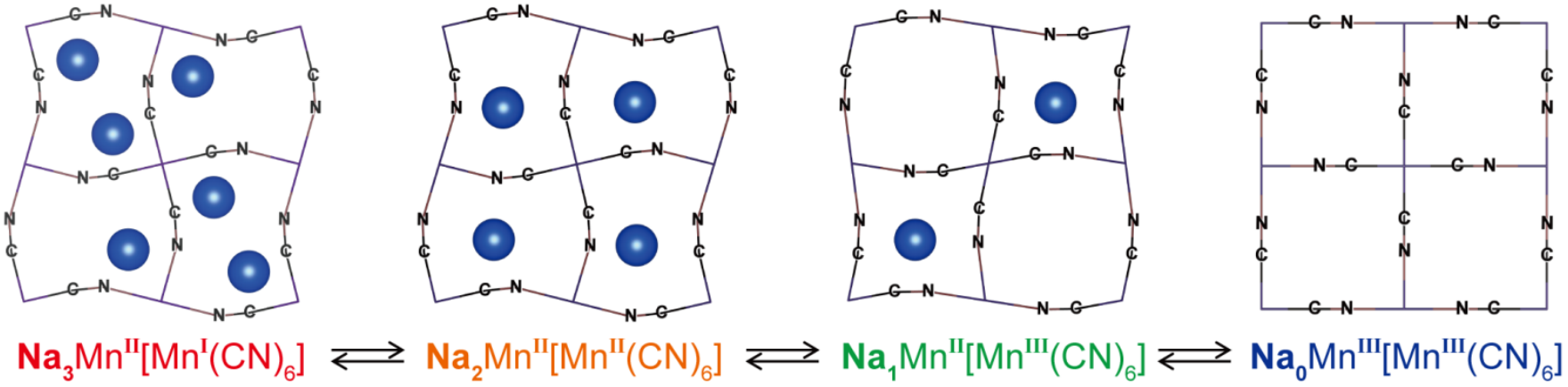
  - Compared to the highest capacity cathode material in Na-ion battery



N. Yabuuchi *et al.*, *Nat. Mater.* **11**, 512, (2012).

Summary

- **In the quest to replace Li-ion batteries in energy storage systems,**
  - New family of the materials offers a lot of opportunities on diverse batteries.
    - Positive electrode material for Na-ion battery (209 mAh/g, 2.7 V vs. Na/Na^{+})



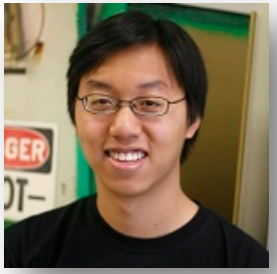
  - MnHCMn represents a novel and scientifically intriguing material that can push forward the development of practical NIBs.

Acknowledgement

– **US Department of Energy (DOE) Office of Electricity Delivery and Energy Reliability in collaboration with the Pacific Northwest National Laboratory**

Prof. Yi Cui

Dr. Mauro Pasta



Richard Wang

Thank you for your kind attention!