BEYOND | Lithium Ion VIII
June 2-4, 2015 · Oak Ridge, TN

Layered Metal Oxide Electrodes for Stationary Sodium-Ion Batteries

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Welcome comments and questions to: yshu@iphy.ac.cn

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Why Room-Temperature Sodium-Ion Batteries??

High energy density

High power density

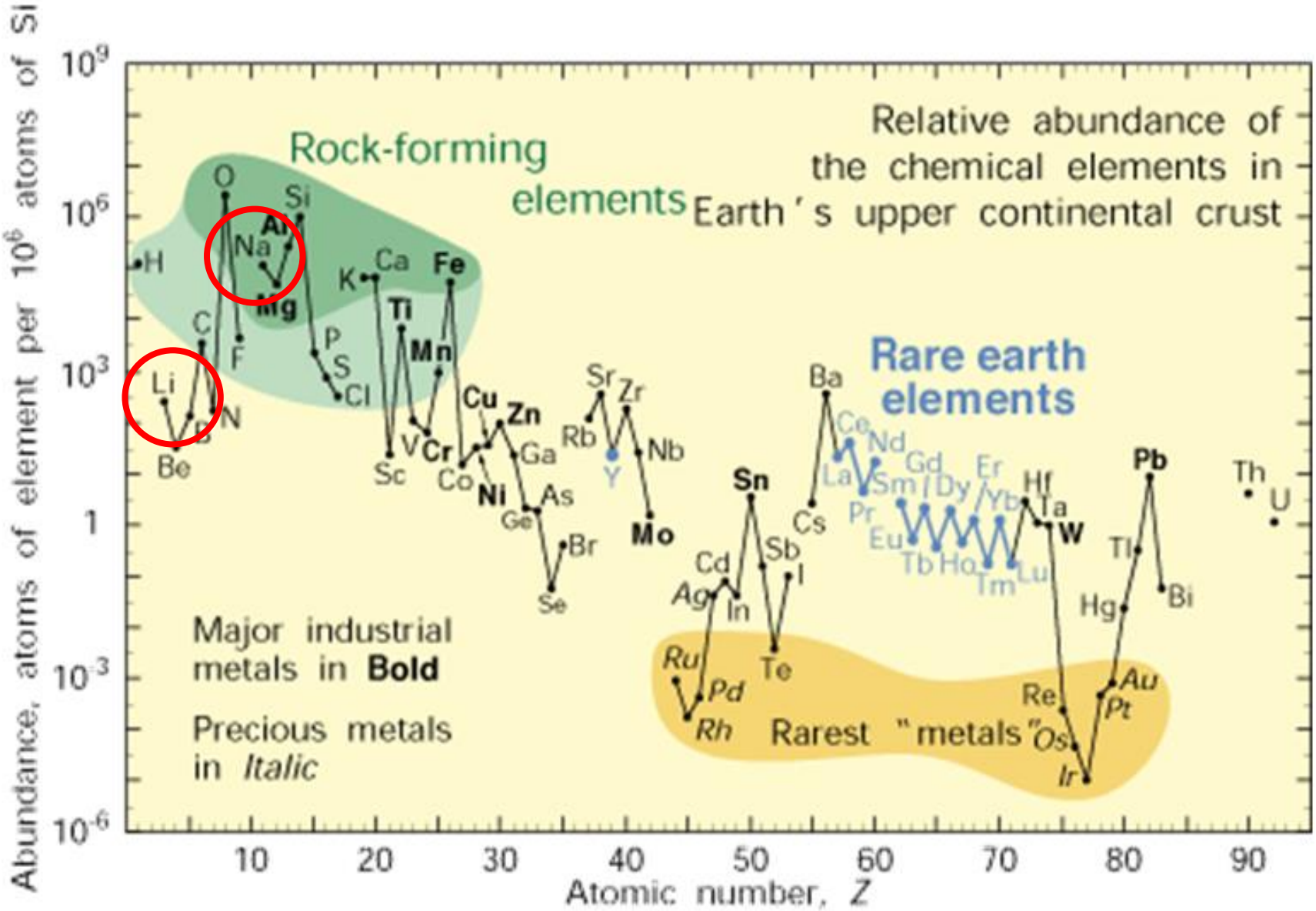
Long cycle life

Requirements of batteries for large-scale energy storage

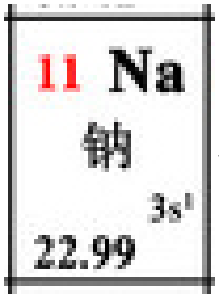
Key parameters of Stationary Batteries：

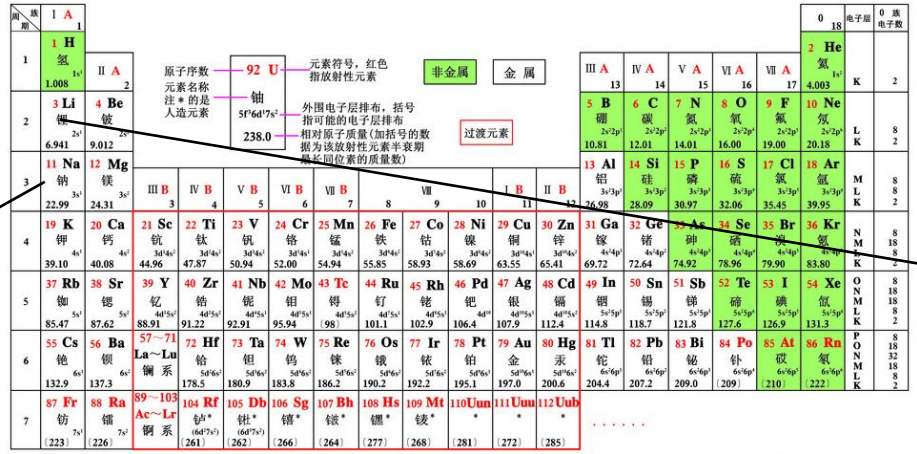
- **Work life： 10-30 years；**
- **Cycle life： > 5000 cycles；**
- **Energy efficiency： ≥ 80%；**
- Self discharge： ≤ 10%/month；
- Work temperature： -20 - 60 ^{o}C；
- Energy density： 40-200 Wh/kg；
- **Low cost, environmental benign & high safety。**

Why Room-Temperature Sodium-Ion Batteries??



Na pk Li





Na

2.75% of Earth's crust

Low price: 2 RMB/kg

"Everywhere"

Al anode current collector: **Yes**

Ionic radius: **97 pm**

Standard potential: **-2.70 V**

Li

0.0065% of Earth's crust

High price: **40 RMB/kg**

70% in S. America

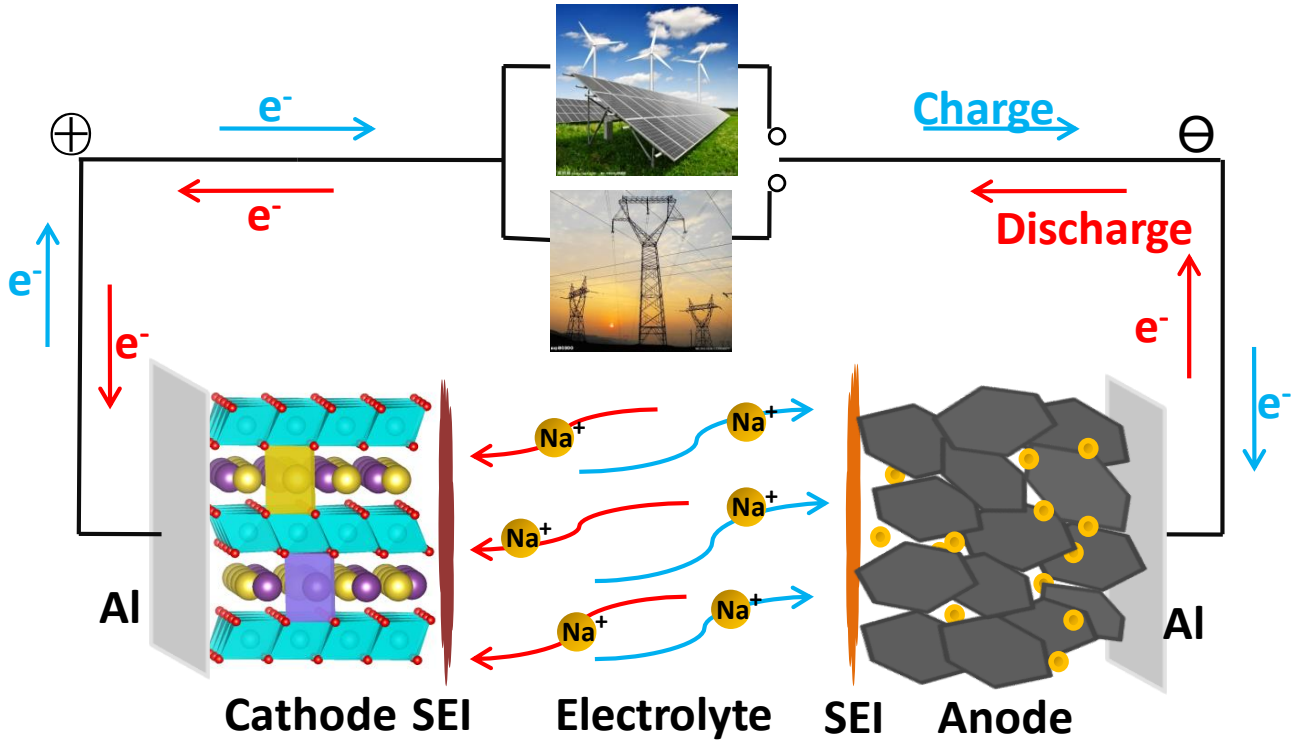
Al anode current collector: **No**

Ionic radius: **68 pm**

Standard potential: **-3.04 V**

√ **Low cost;** × **Lower energy density compared with Li system.**

Working principle: similar to Li-ion Batteries

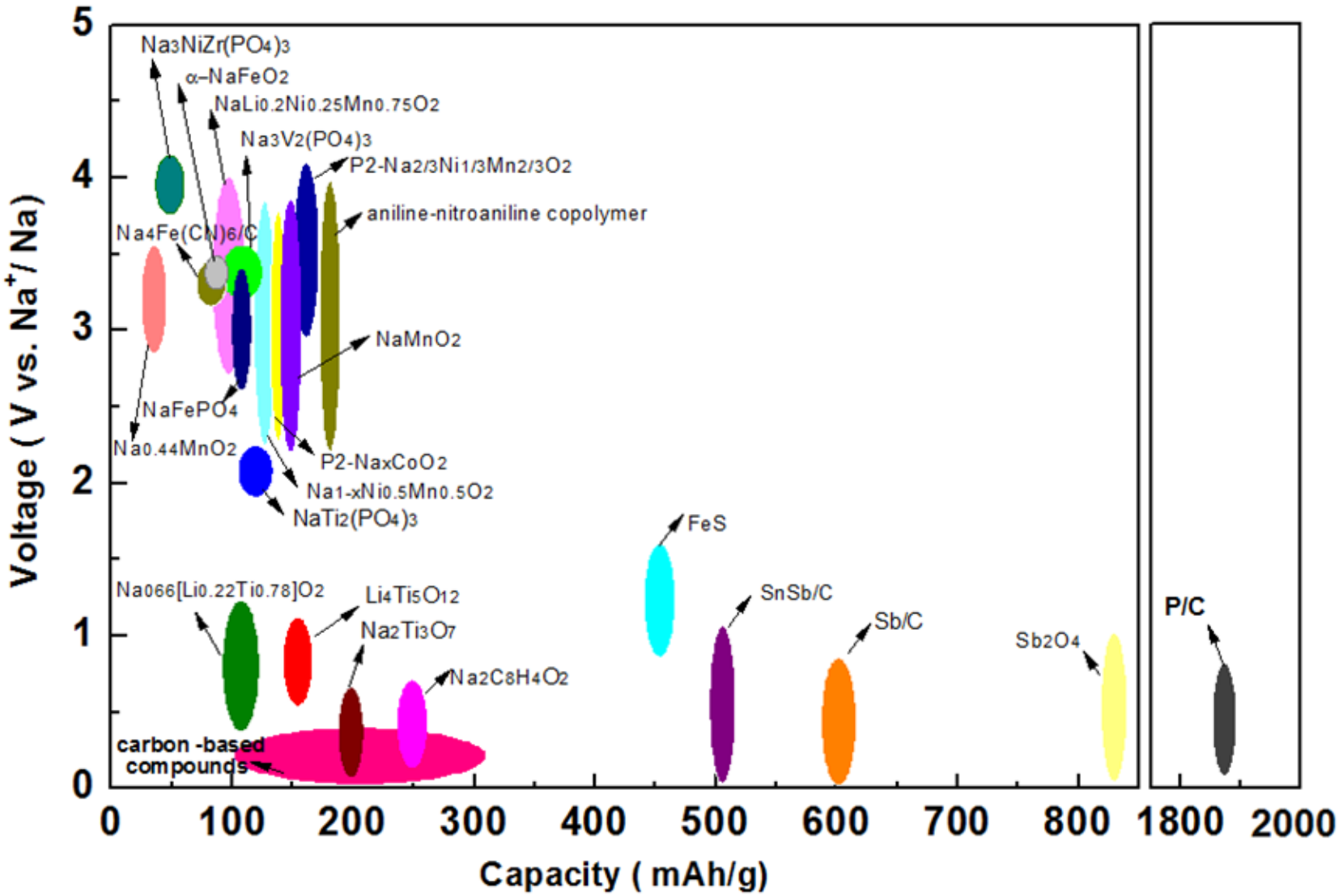


Insertion host

"Rocking chair"
M. Armand, 1972

- Transport of electron *(bulk, surface, interface)*
- Transport of ion (Na^+) *(bulk, surface, interface)*
- Charge Transfer *(interface/bulk ?)*
- Storage of both *(bulk, surface, interface)*
- Phase transition *(bulk)*
- Solid Electrolyte Interphase (SEI) reaction *(surface)*

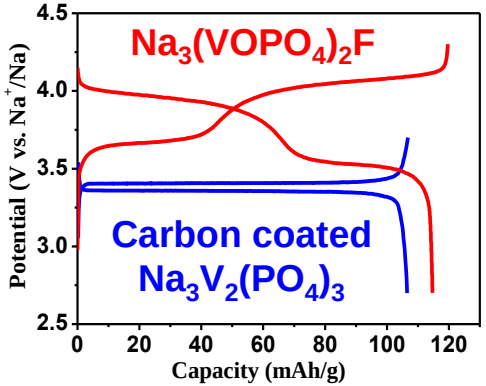
Many Interesting Materials for Sodium-Ion Batteries



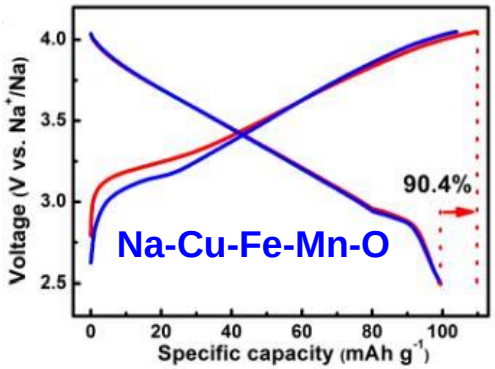
Y. -S. Hu, et al.* Energy Environ. Sci., 2013, 6, 2338.

New Materials Developed from IoP-CAS

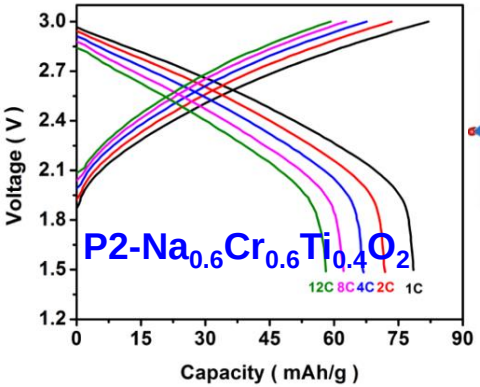
We have been working on sodium-ion batteries since May 2011.



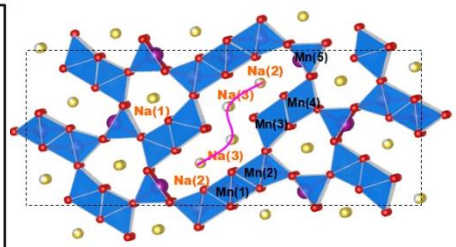
EC 2012; AEM 2013; AFM 2014
CC 2015, Angew Chem 2015



CPB 2014; CPB 2015;
Advanced Science 2015

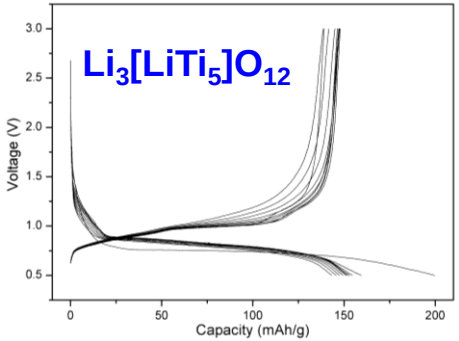


Nature Commun 2015

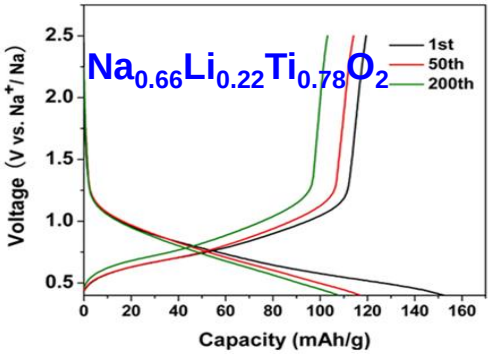


Nature Commun 2015

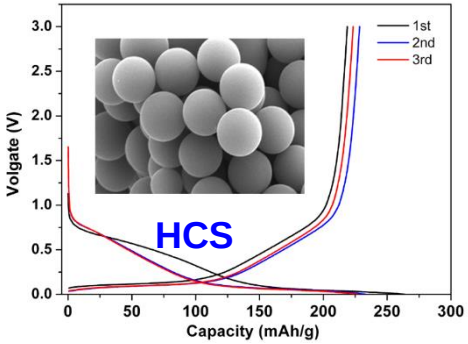
Polyanions → ***Layered metal oxides*** → ***Tunnel oxides***



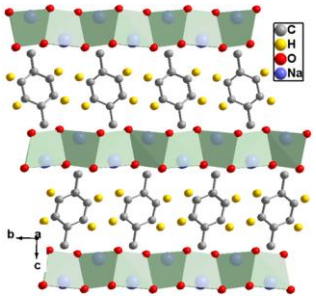
CPB 2012; NL 2013
Nature Commun 2013



Nature Commun 2013



JMCA 2015



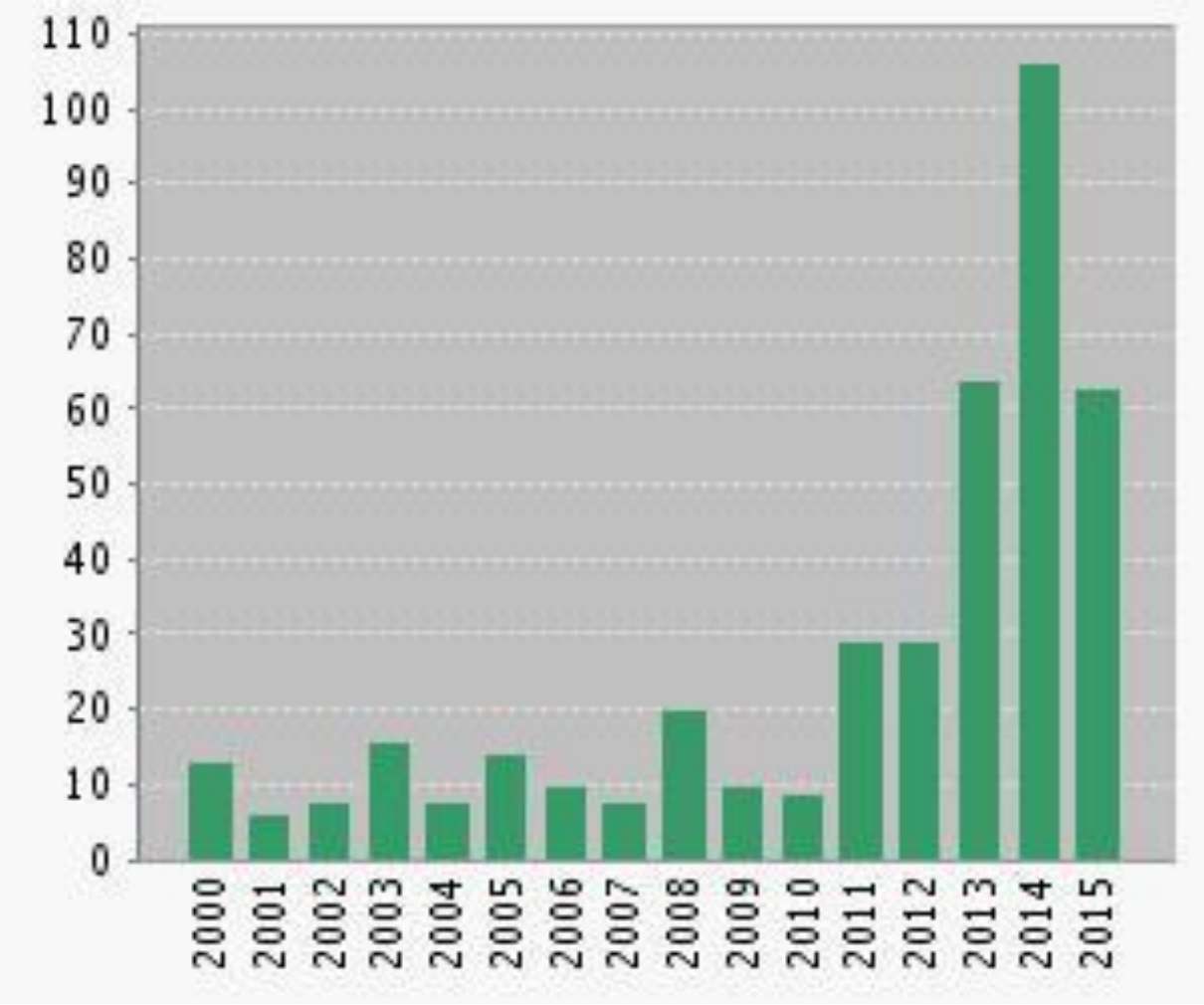
Organic electrodes

AEM 2012; JMCA 2015
Science Advances 2015

Spinel oxide → ***Layered metal oxides*** → ***Carbon*** → ***Organic materials***

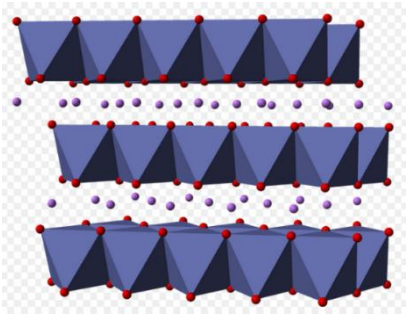
Publications for Sodium Layered Oxide between 2000-2015

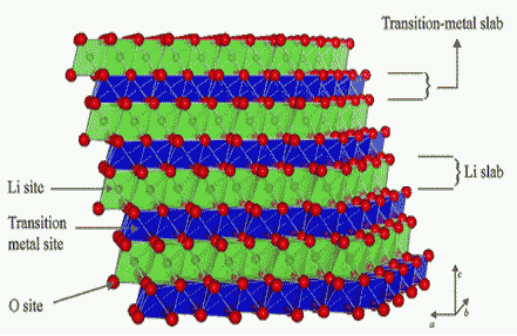
From Web of Science

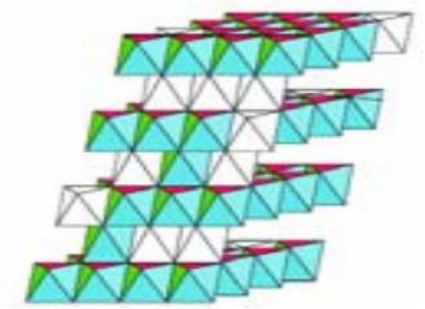


Easy synthesis, High reversibility, High energy density

Layered Oxide Cathodes for Lithium-Ion Batteries



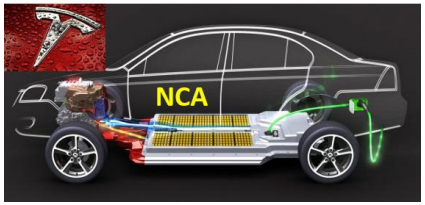




$LiCoO_2$ | **NCM/NCA** | **$Li_{1+x}Ni_yCo_zMn_mO_{2-n}$**

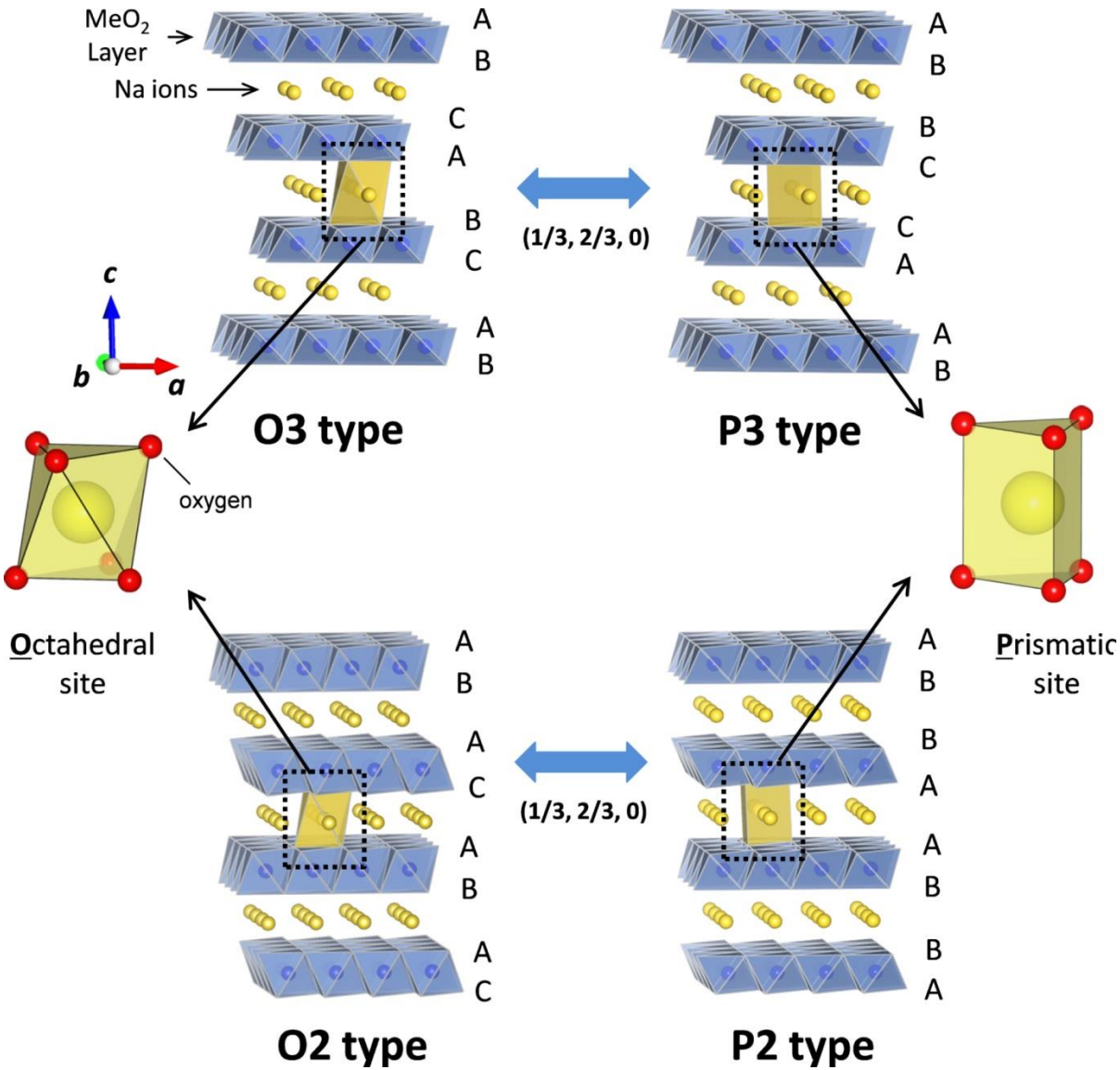
1980 → **18650 battery Portable Devices**

1993 → **power batteries for electric vehicles**



2004 → **next power batteries for electric vehicles**

Layered Oxide Cathodes for Sodium-Ion Batteries



O3: NaxMO2 (x～1)

Space Group: R-3m

ABCABC…

P2:NaxMO2 (x<1, 2/3)

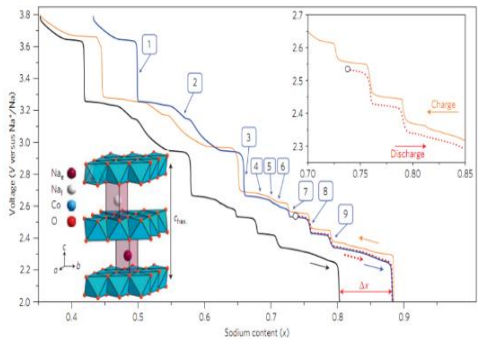
Space Group: P63/mmc

ABBA…

C. Delmas, et al., *Solid State* Ionics, 1981, 3-4, 165.

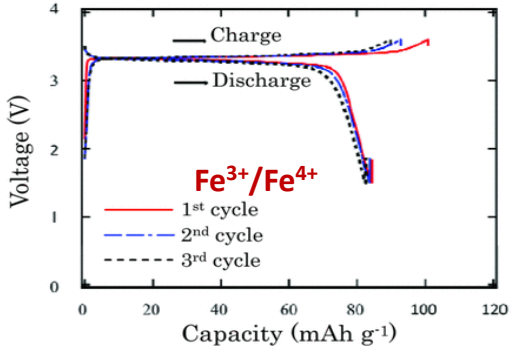
S. Komaba, et al. *Chem. Rev.* 2014, 114, 11636.

Layered Oxide Cathodes for Sodium-Ion Batteries



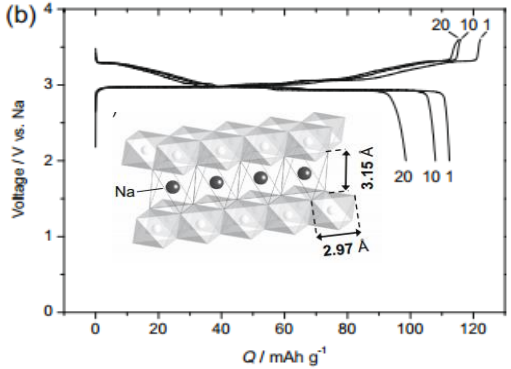
Na_xCoO_2

C. Delmas, DOI: 10.1038/NMAT2920



$NaFeO_2$

S-Okada, DOI: 10.1149/2.007305jes

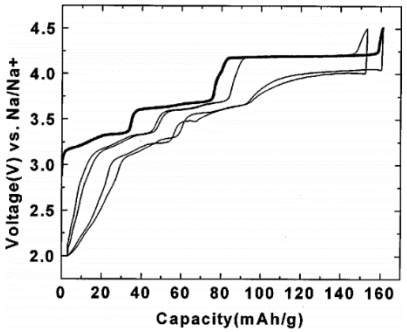


$NaCrO_2$

S. Komaba, Electrochem. Commun.2010,12, 355

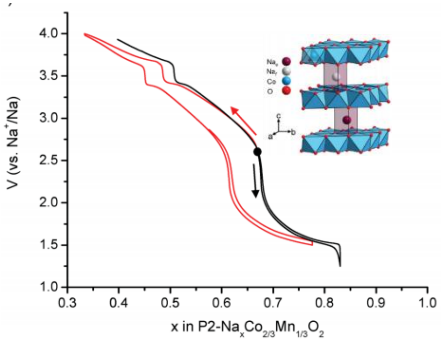
O3-$NaCoO_2$ (1980) $NaNiO_2$ (1982) $NaMnO_2$ (1985) $NaFeO_2$ (2006) $NaCrO_2$ (2010)

P2-$Na_{0.74}CoO_2$ $Na_{0.67}MnO_2$ $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ $Na_x[Li_yNi_zMn_{1-y-z}]O_2$ $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$



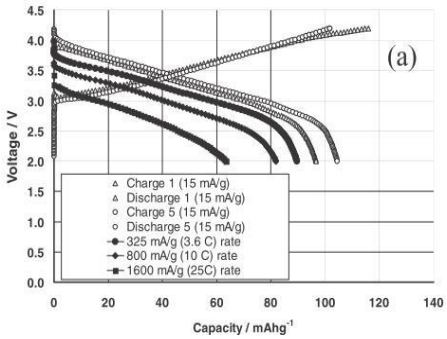
$P2\text{-}Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$

J. R. Dahn, *JES* 2011, 148, A1225



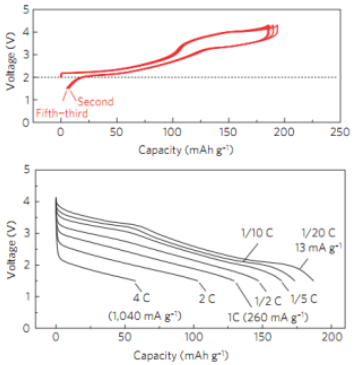
$P2\text{-}Na_{2/3}Co_{2/3}Mn_{1/3}O_2$

C. Delmas, Dalton Trans., 2011, 40, 9306



$P2\text{-}Na_{0.85}Li_{0.17}Ni_{0.21}Mn_{0.64}O_2$

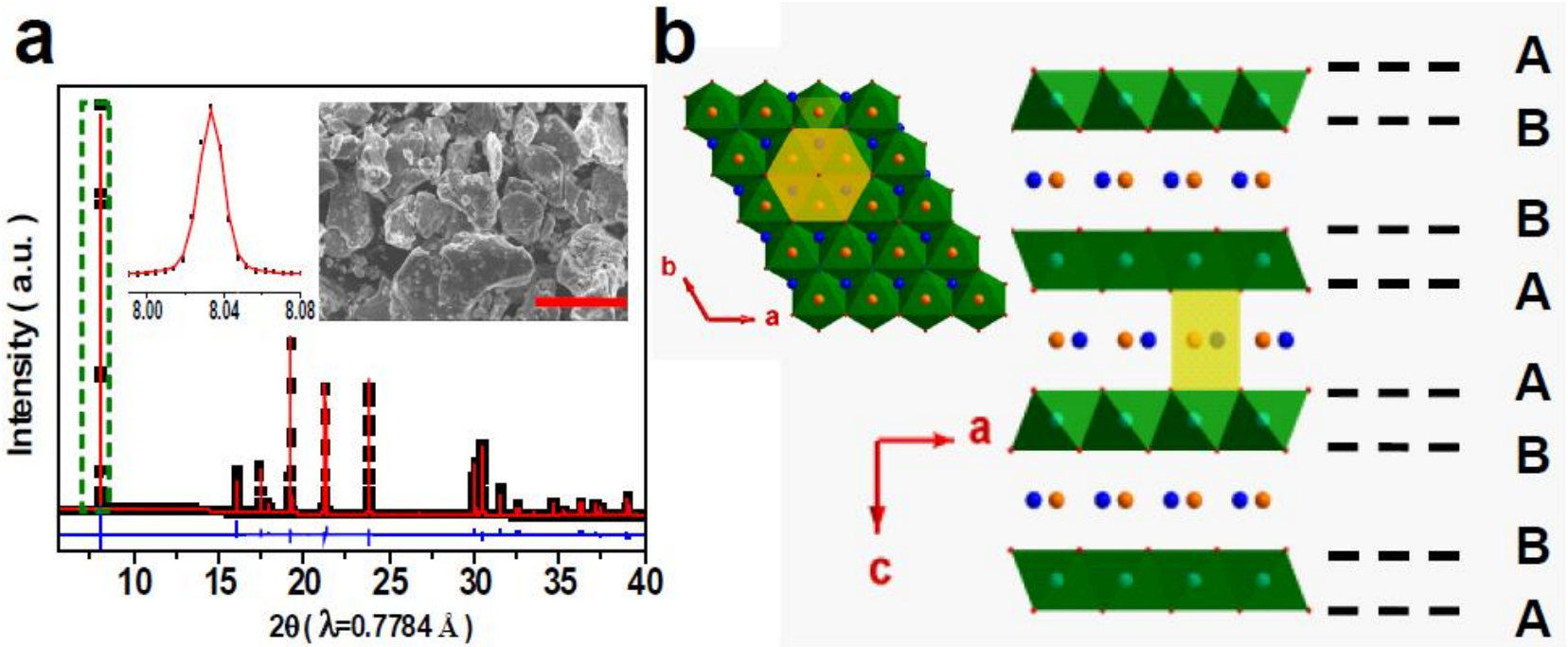
C. S. Johnson, AEM, 2011, 1, 333



$P2\text{-}Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$

S. Komaba, DOI: 10.1038/NMAT3309

Layered Oxide Anode: $Na_{0.66}[Li_{0.22}Ti_{0.78}]O_2$



Space group: $P6_3/mmc$;

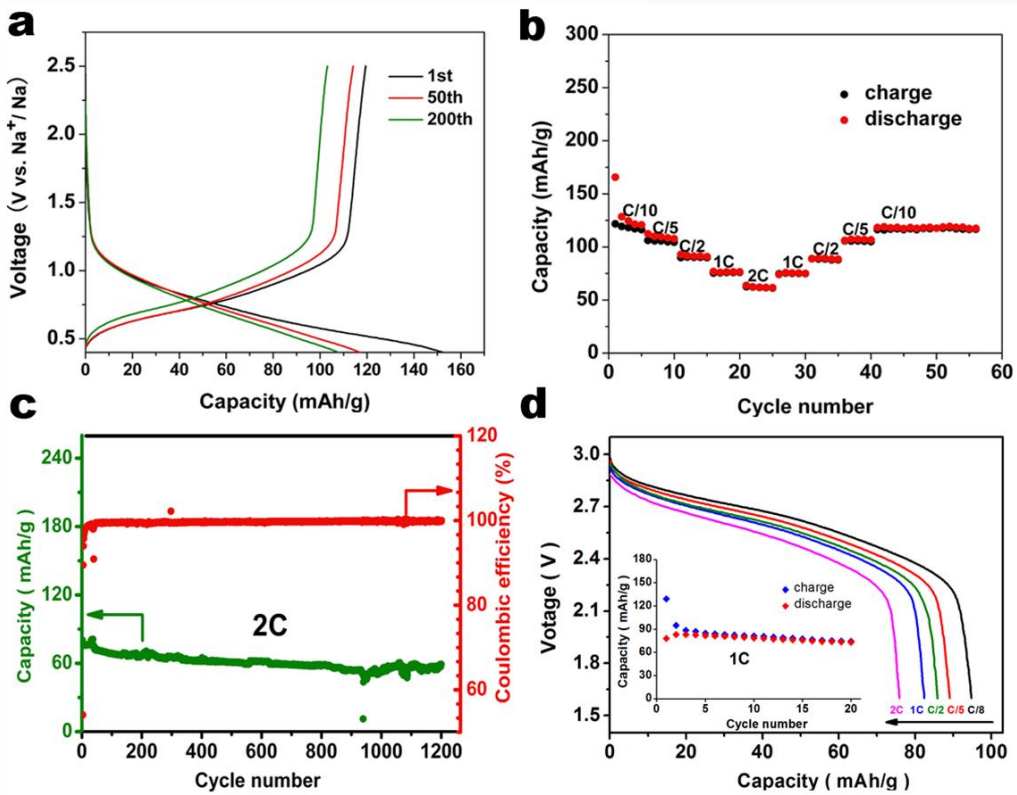
Crystal structure : Layered P2;

Lithium position: TM layer;

Sodium position: Trigonal prismatic sites， 2d (0.425)， 2b (0.211).

Particle size: 10-15 μm.

Layered Oxide Anode: $Na_{0.66}[Li_{0.22}Ti_{0.78}]O_2$



Volume change: -0.77%

Reversible capacity: 116 mAh/g, 0.34 Na insertion per formula unit;

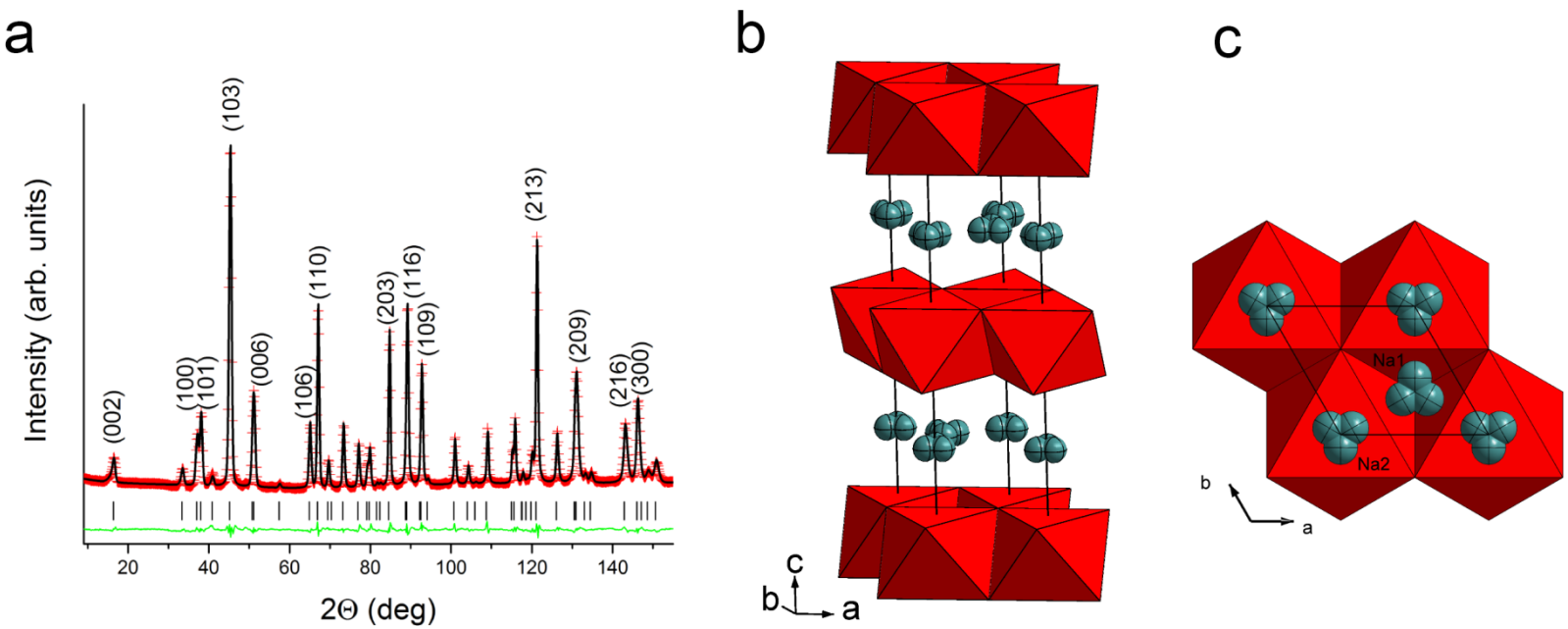
Discharge/charge curves: Sloped behavior, like single-phase reaction;

Na storage voltage: 0.75 V;

Long-term cyclability: 75% capacity retention for over 1200 cycles.

Y. S. Wang, X. Q. Yu, S. Y. Xu, J. M. Bai, R. J. Xiao*, Y.-S. Hu*, H. Li, X. -Q. Yang, L. Q. Chen, X. J. Huang, ***Nature Communications*** 2013, 4, 2365.

Layered Oxide Cathode and Anode: $Na_{0.6}[Cr_{0.6}Ti_{0.4}]O_2$



Space group : **$P6_3/mmc$;**

Crystal structure : **Layered P2;**

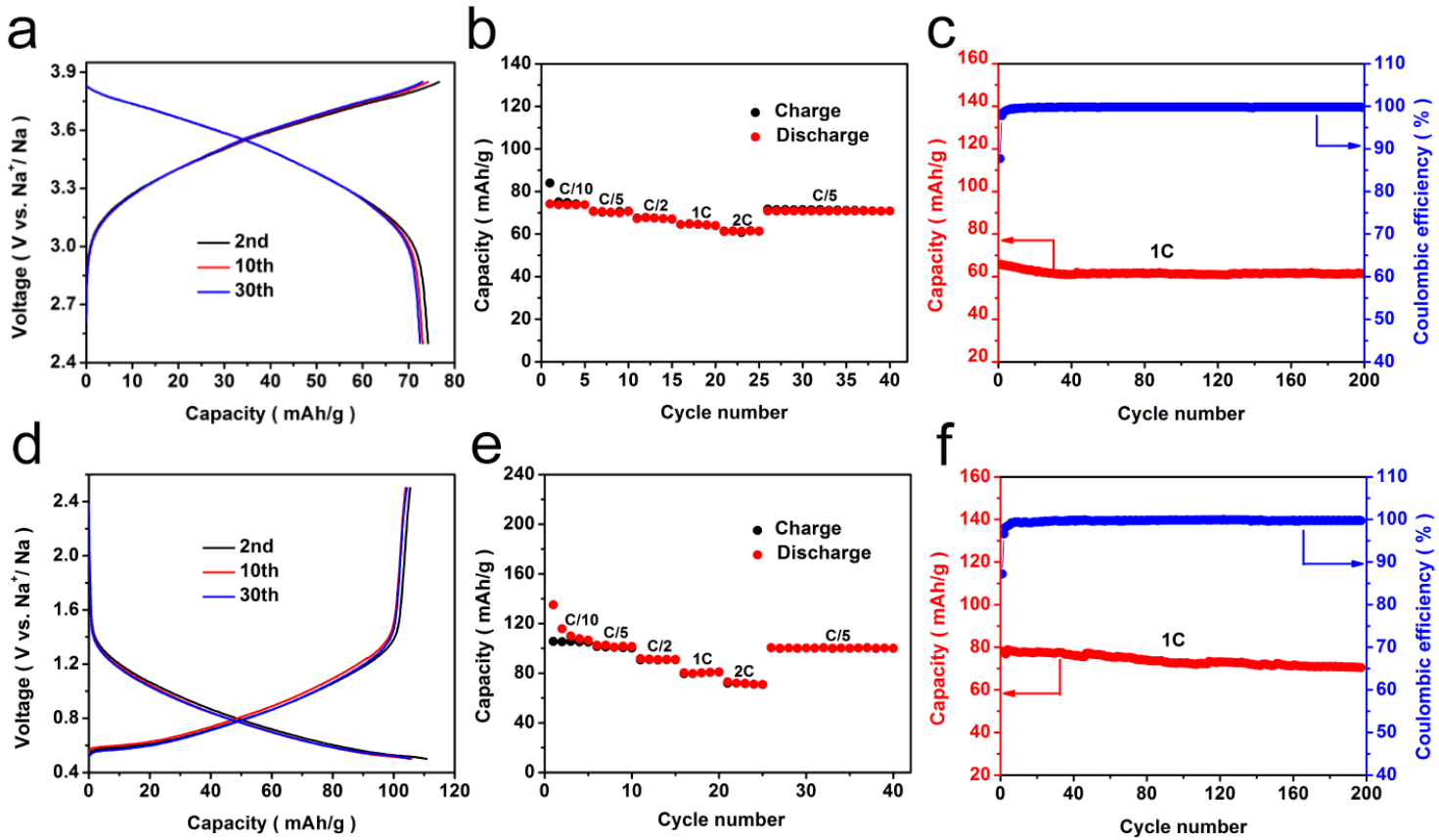
Cr/Ti position: **TM layer;**

Sodium position: **Trigonal prismatic sites，6h (0.1316)，6h (0.0684).**

Particle size : **1-5 μm.**

Dr. Avdeev performed the NPD.

Layered Oxide Cathode and Anode: $Na_{0.6}[Cr_{0.6}Ti_{0.4}]O_2$

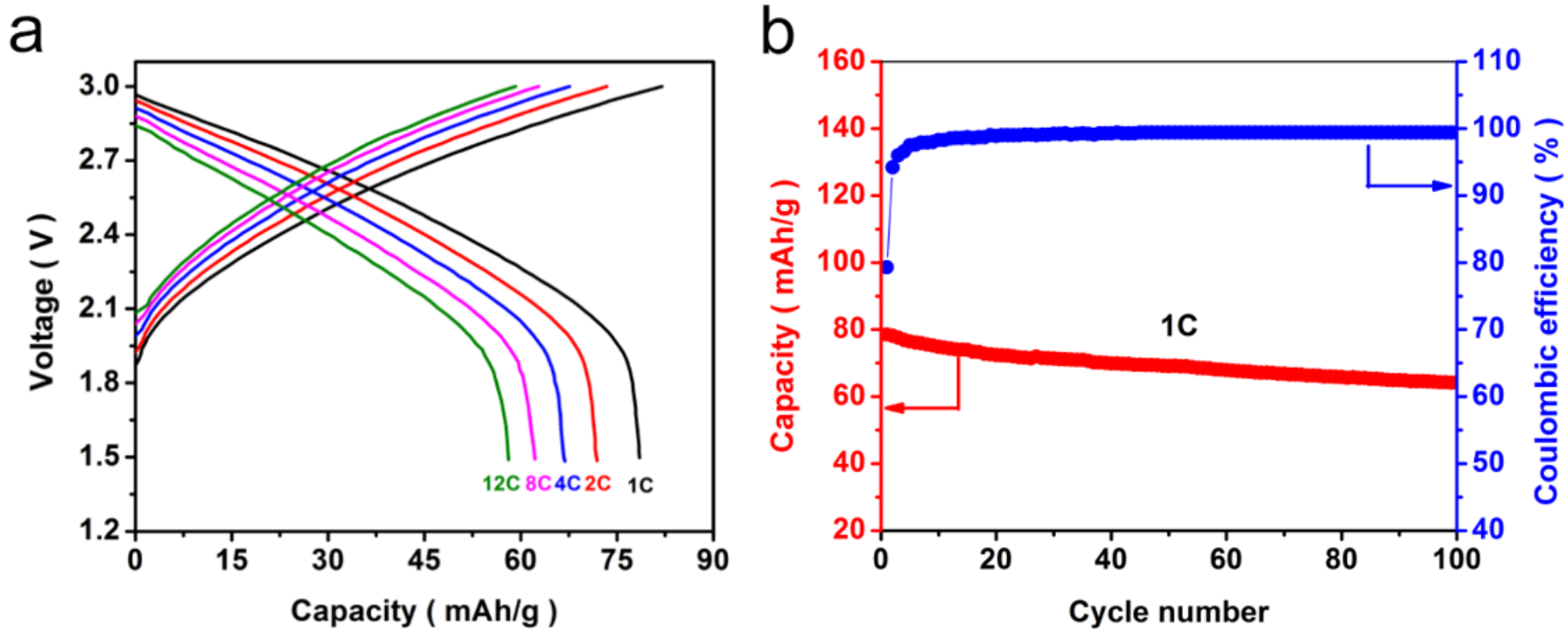


Na storage voltage : **Cathode: 3.5 V;** **Anode: 0.8 V.**

Rate: **Cathode: 2C 81%** **Anode: 2C 65%**

Long-term cyclability: Cathode: 94%, 200 cycles; Anode: 90.4%, 200 cycles.

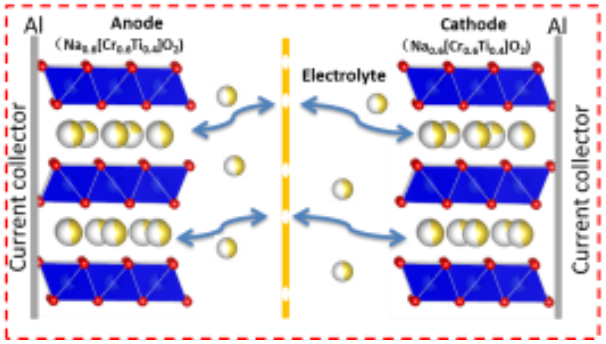
Layered Oxide Cathode and Anode: $Na_{0.6}[Cr_{0.6}Ti_{0.4}]O_2$



Average operation voltage：2.53 V

Energy density: ～ 90 Wh/kg

Rate：12C, 68%

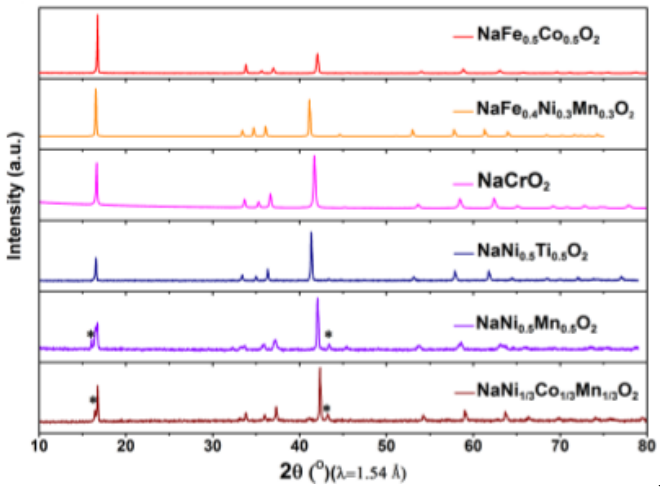


Y. S. Wang, R. J. Xiao, Y.-S. Hu*, M. Avdeev*, L. Q. Chen, ***Nature Communications*** 2015, 6, 6954.

Layered Oxide Cathodes for Practical Application:

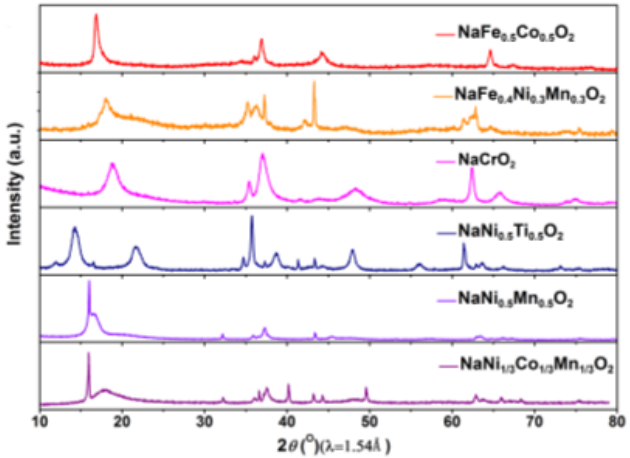
Challenge I: not stable in air

O3

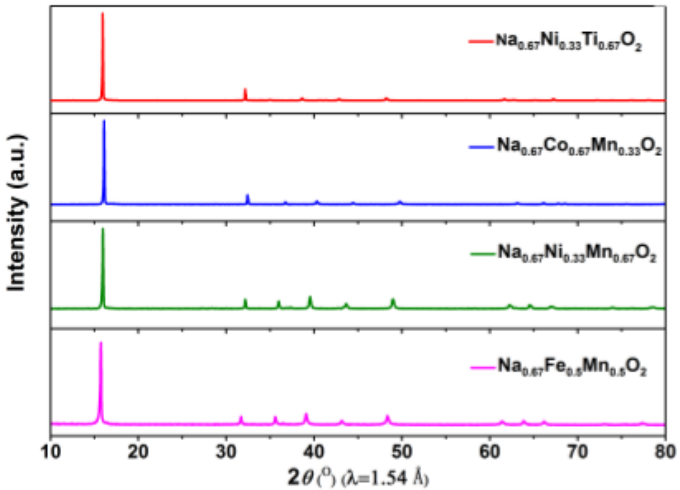


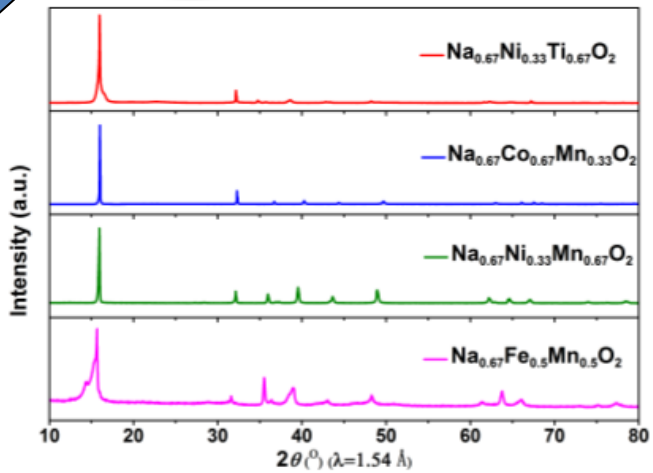
Unstable

Soaked in H_2O



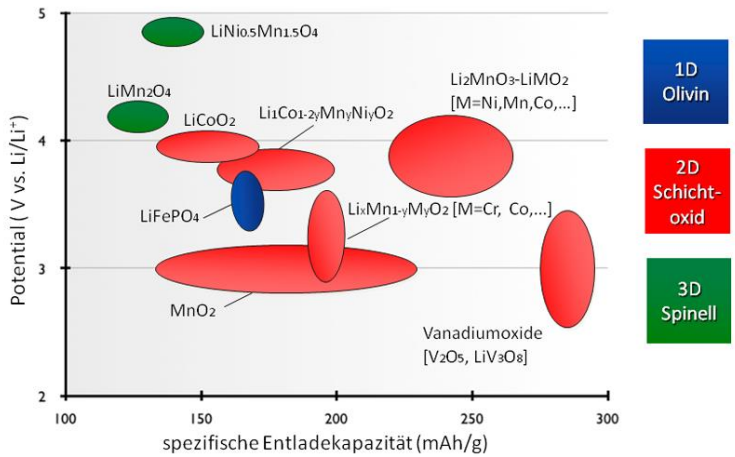
P2

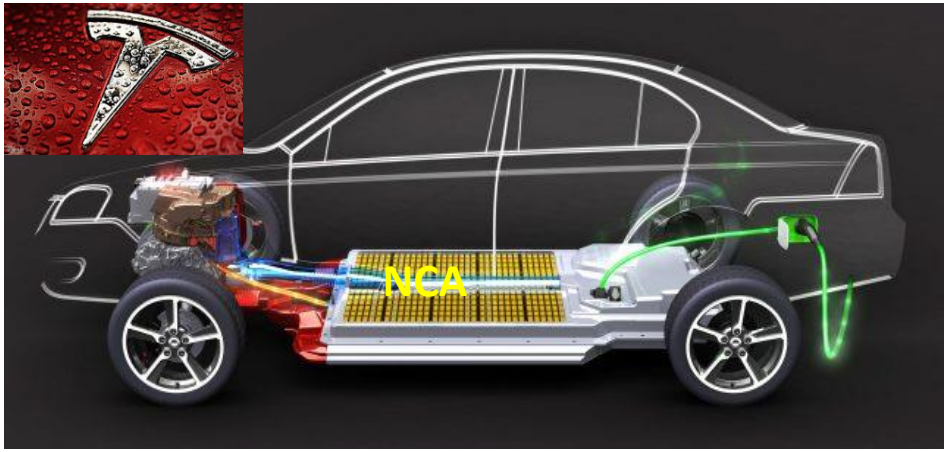


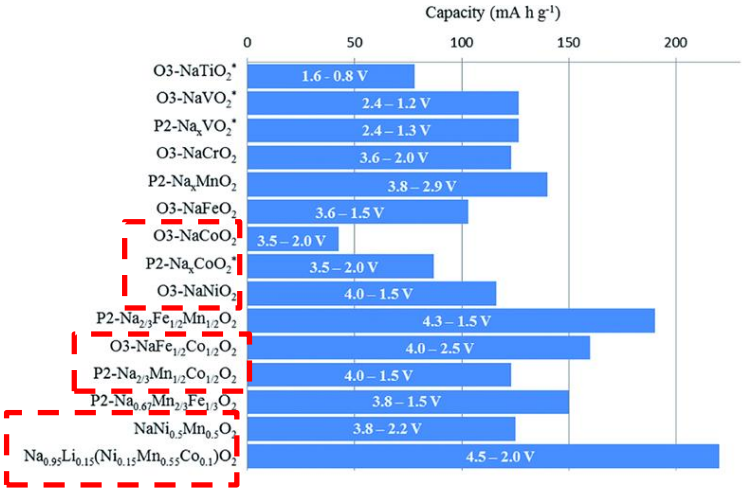


Layered Oxide Cathodes for Practical Application:

Challenge II: containing Ni or Co



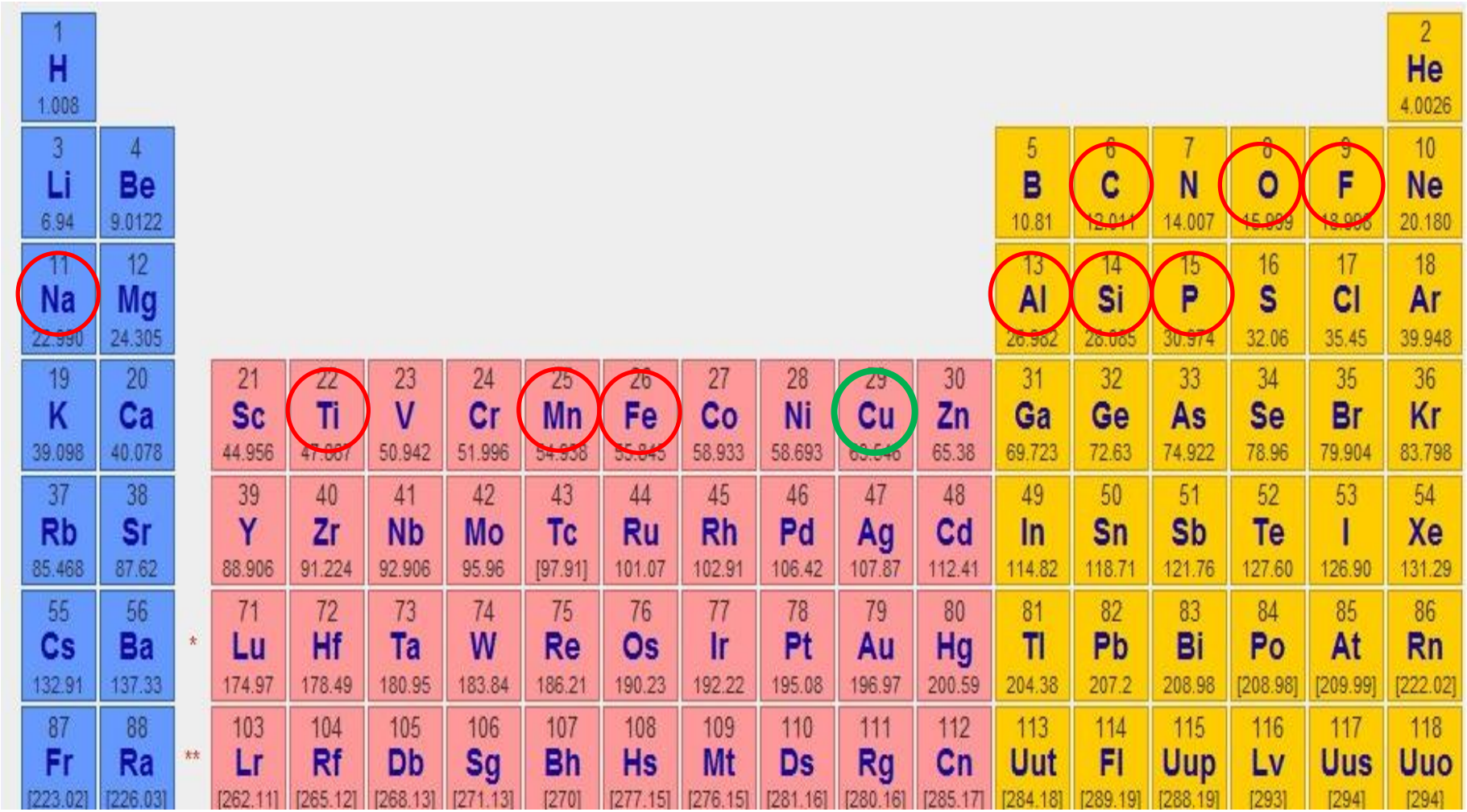




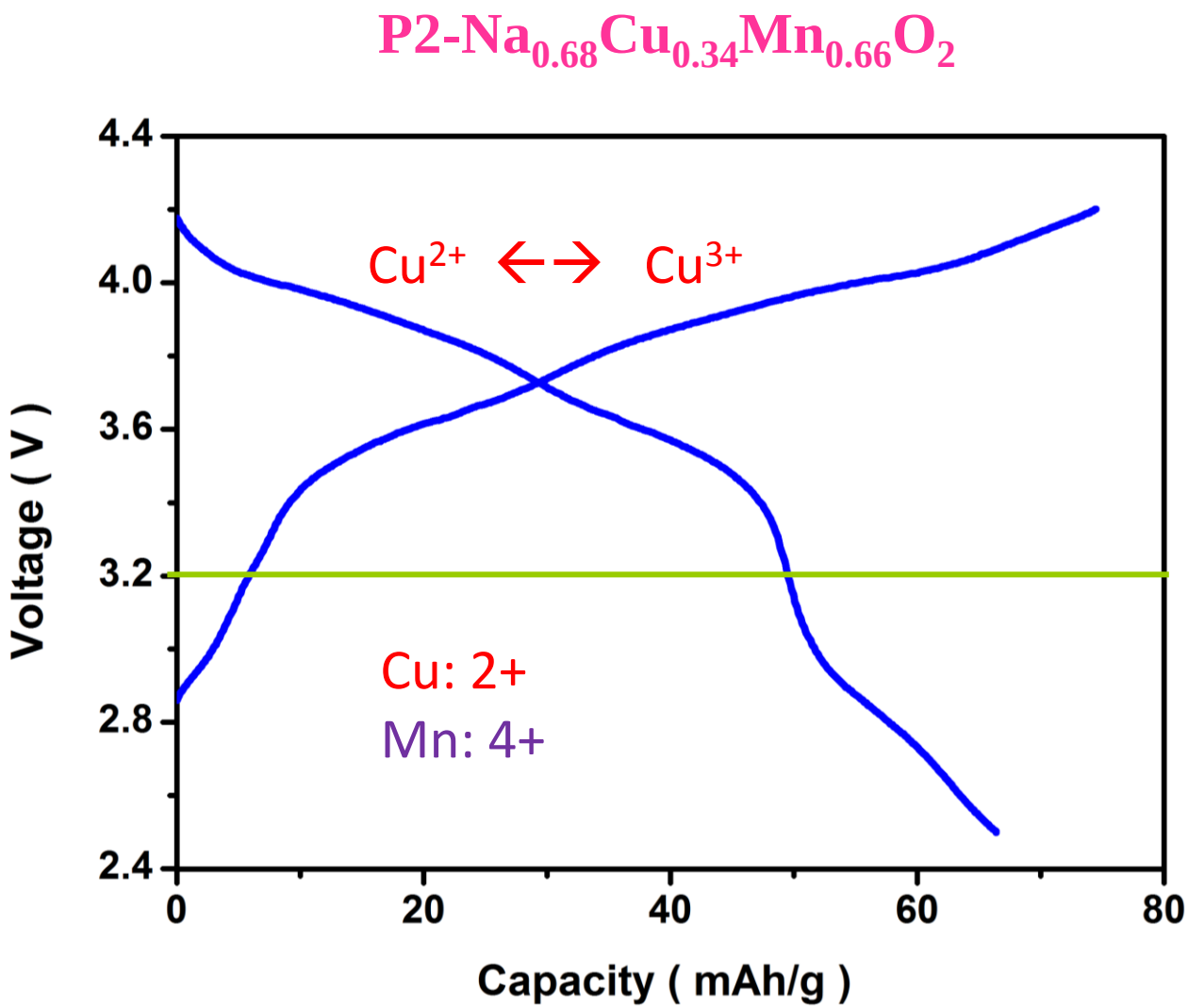
	Price (RMB)		Price (RMB)
Na_2CO_3	2000/t	Fe_2O_3	5400/t
NiO	90000/t	Mn_2O_3	5600/t
CoO	185000/t		

Need to explore NEW redox chemistry ! !

Explore new redox chemistry

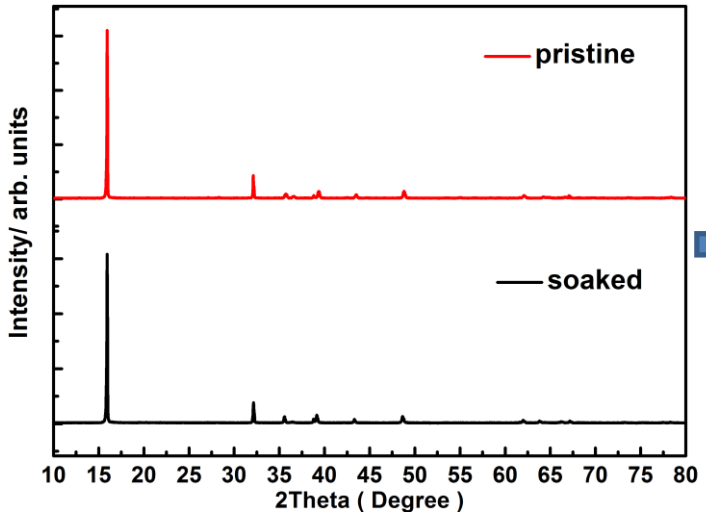


Novel reversible Cu^{2+}/Cu^{3+} redox couple



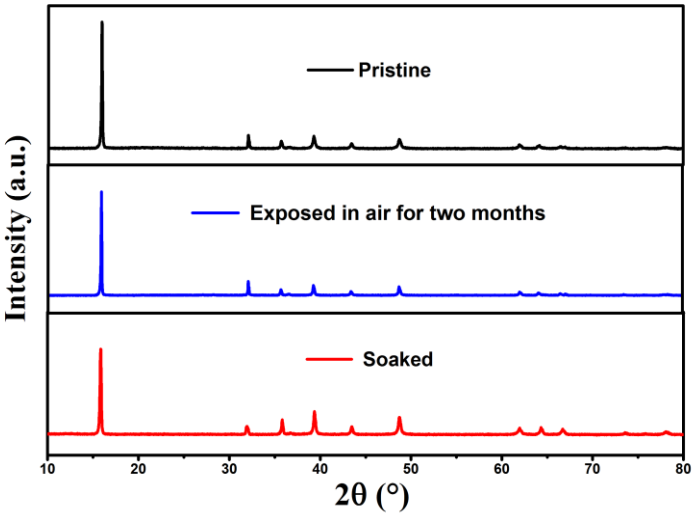
Hu Y-S* et al. Novel copper redox-based cathode materials for room-temperature sodium-ion batteries. ***Chinese Physics B*** 23, 118202 (2014).

Air-stable copper-based P2-$Na_{7/9}[Cu_{2/9}Fe_{1/9}Mn_{2/3}]O_2$



Fe

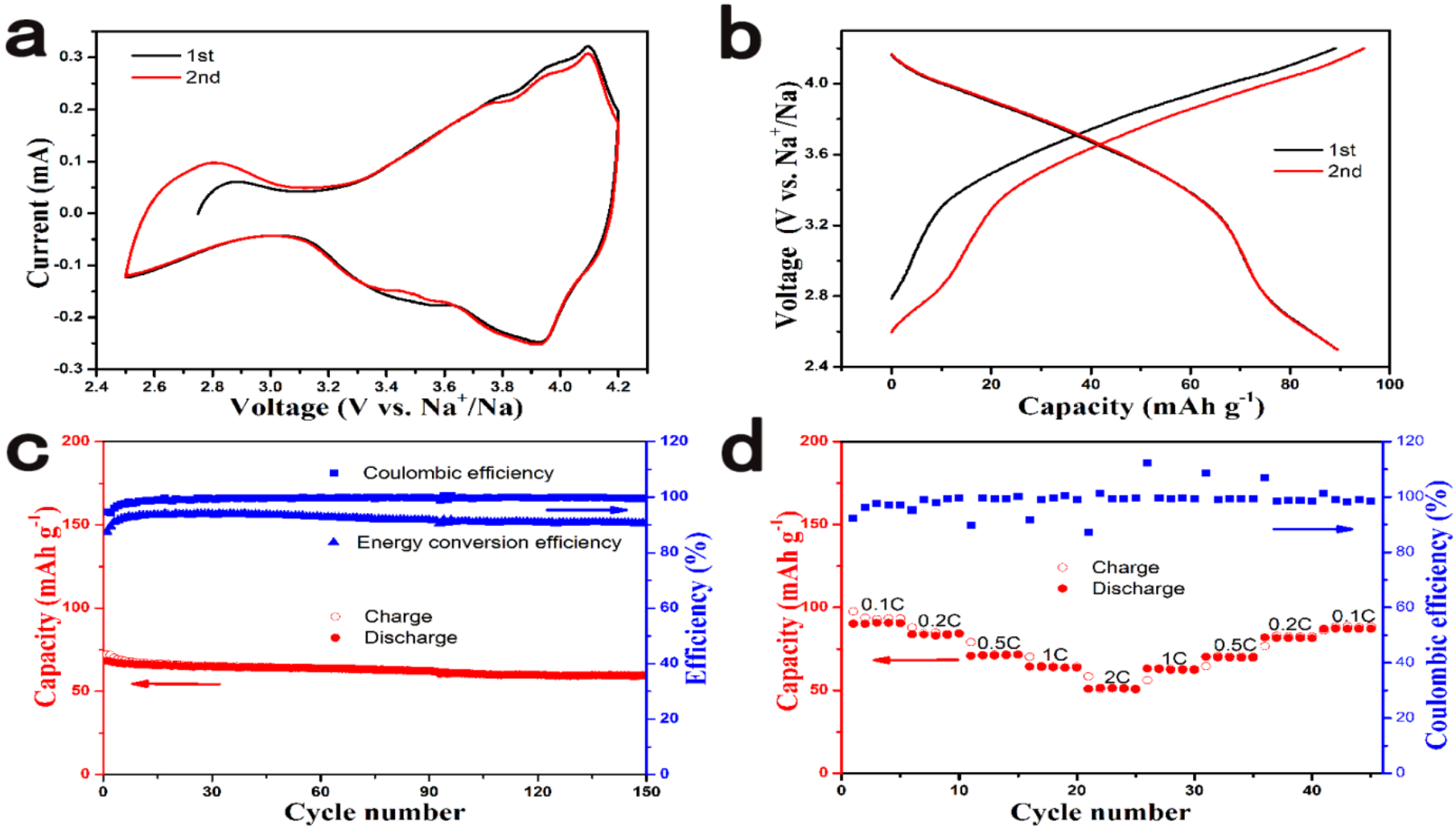
Improving sodium content by doping



$P2\text{-}Na_{2/3}Cu_{1/3}Mn_{2/3}O_2$ → $P2\text{-}Na_{7/9}Cu_{2/9}Fe_{1/9}Mn_{2/3}O_2$

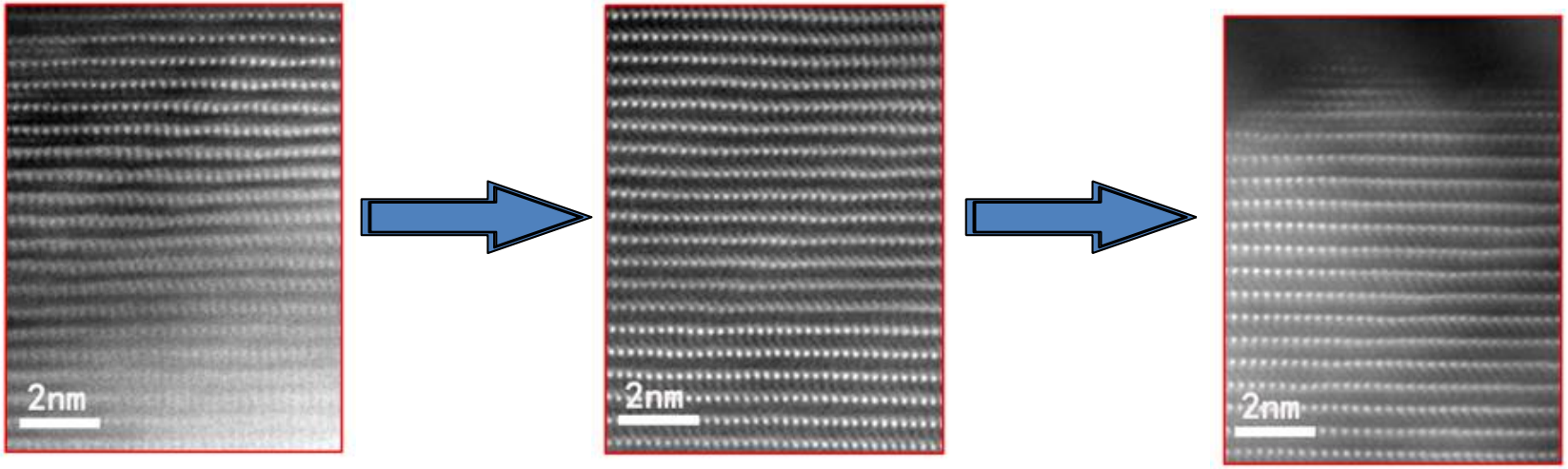
	Price (RMB)		Price(RMB)
Na2CO3	2000/t	CuO	42000/t
NiO	90000/t	Fe2O3	5400/t
CoO	185000/t	Mn2O3	5600/t

Air-stable copper-based P2-$Na_{7/9}[Cu_{2/9}Fe_{1/9}Mn_{2/3}]O_2$

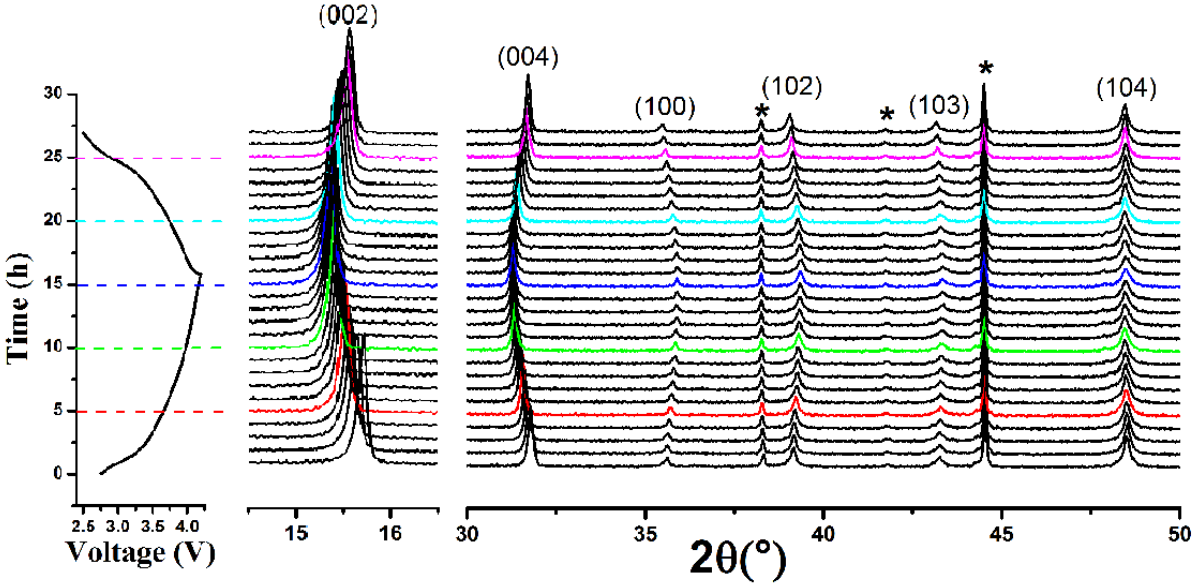


Performance from half cells

Air-stable copper-based P2-$Na_{7/9}[Cu_{2/9}Fe_{1/9}Mn_{2/3}]O_2$



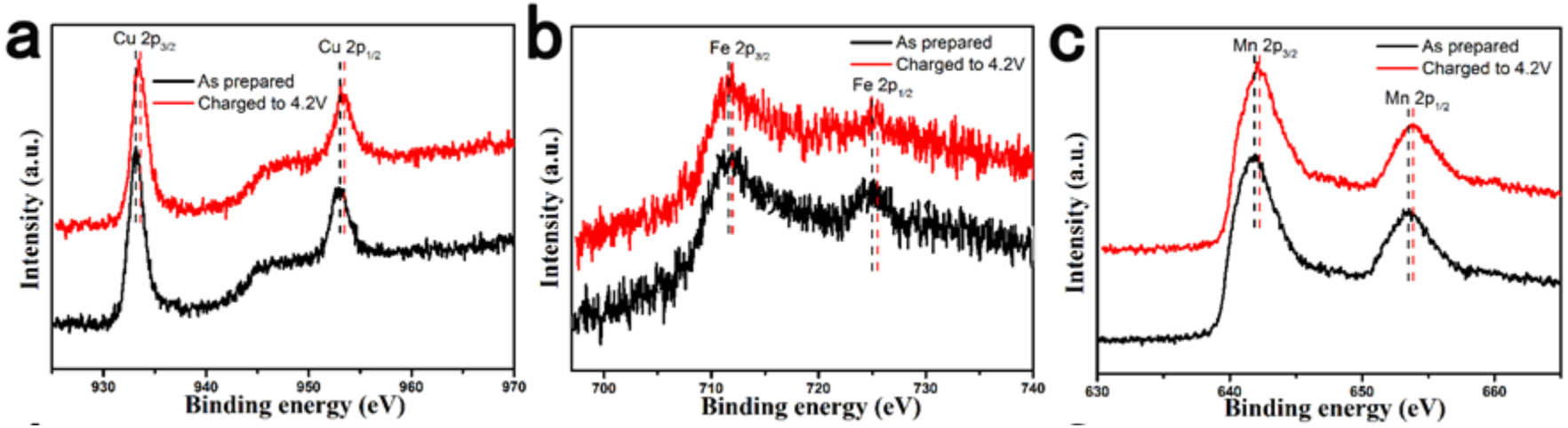
The pristine material The charged state The discharged state



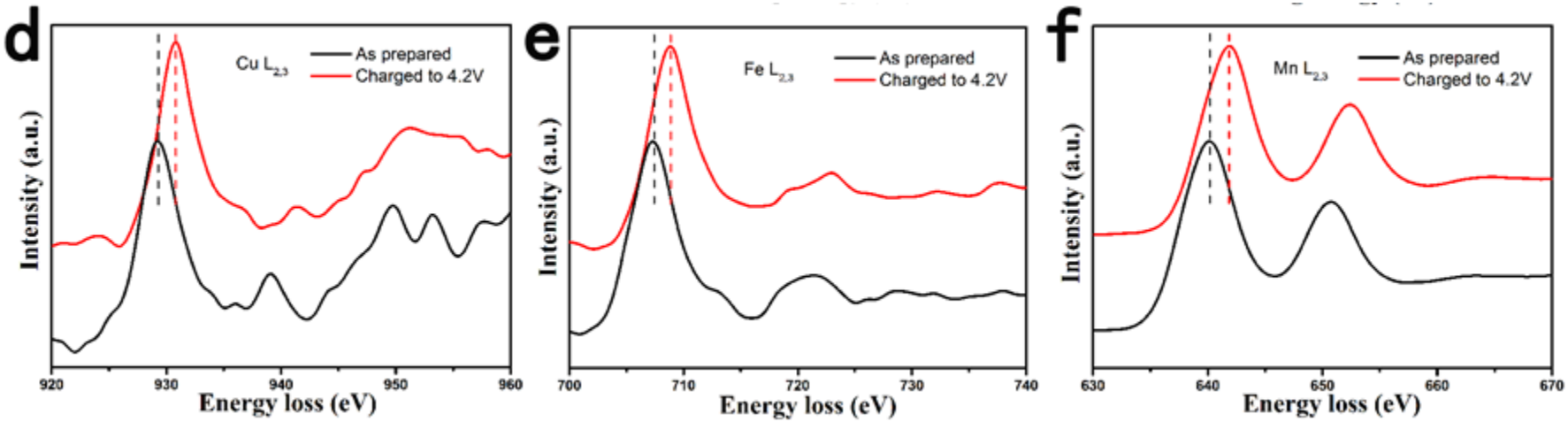
Single phase

Volume change: 1.32%

Air-stable copper-based P2-$Na_{7/9}[Cu_{2/9}Fe_{1/9}Mn_{2/3}]O_2$

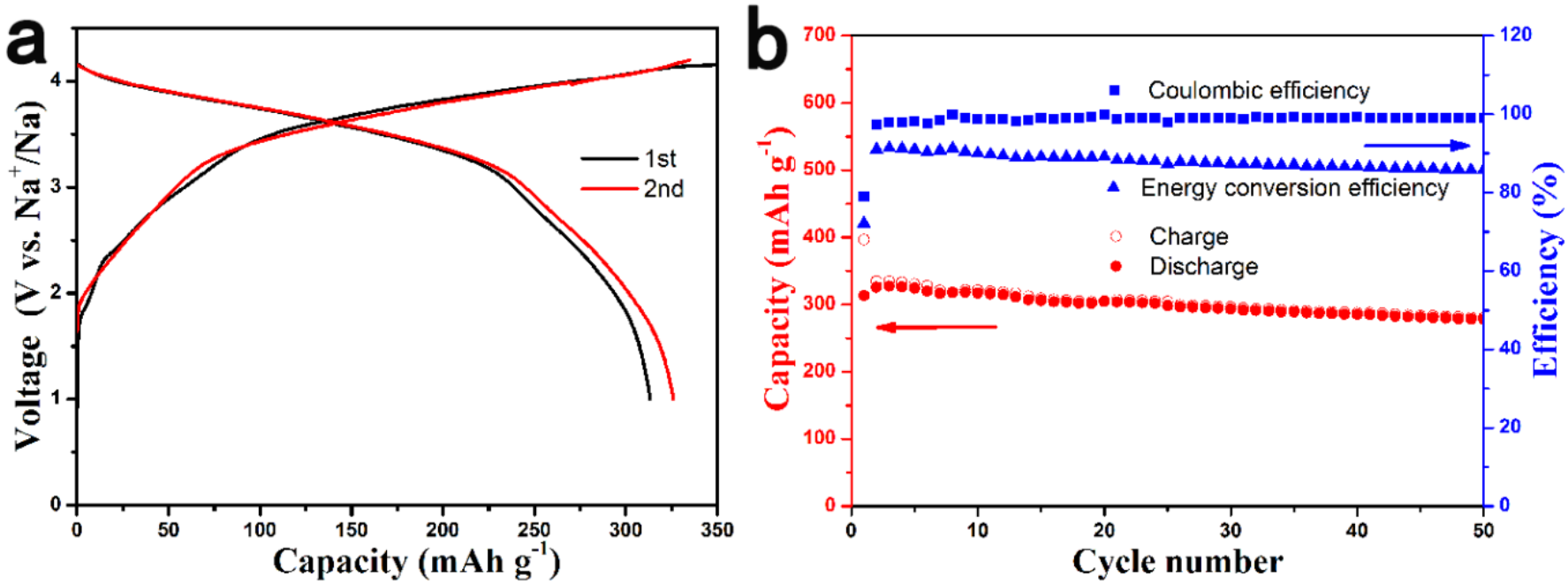


XPS



EELS

Air-stable copper-based P2-$Na_{7/9}[Cu_{2/9}Fe_{1/9}Mn_{2/3}]O_2$



The full cell with hard carbon as anode

Average operation voltage：3.5 V

Energy density: ～ 190 Wh/kg

Energy conversion efficiency：85%

Y. M. Li, Z. Yang, S. Xu, L. Mu, L. Gu*, Y.-S. Hu*, H. Li, L. Q. Chen, ***Advanced Science*** 2015, 1, doi: 10.1002/advs201500031.

Concluding remarks

- Sodium-ion batteries are intentionally developed for large-scale electrical energy storage;
- Layered oxides are important electrodes for SIB due to their high energy density…
- Most of them contain Ni or Co and are not stable;
- We discover the high reversibility of Cu^{2+}/Cu^{3+} redox couple in Na-containing layered oxides and design new air-stable and Ni-/Co-free cathodes for SIB.

Thank you for your kind attention!