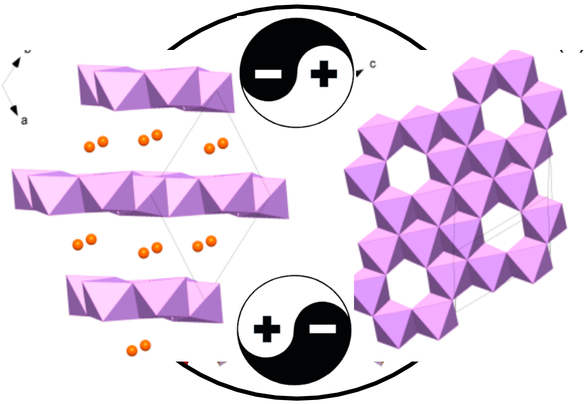
Sodium Manganese Oxide ($Na_2Mn_3O_7$) As A Versatile Battery Insertion Material



Dr. Prabeer Barpanda

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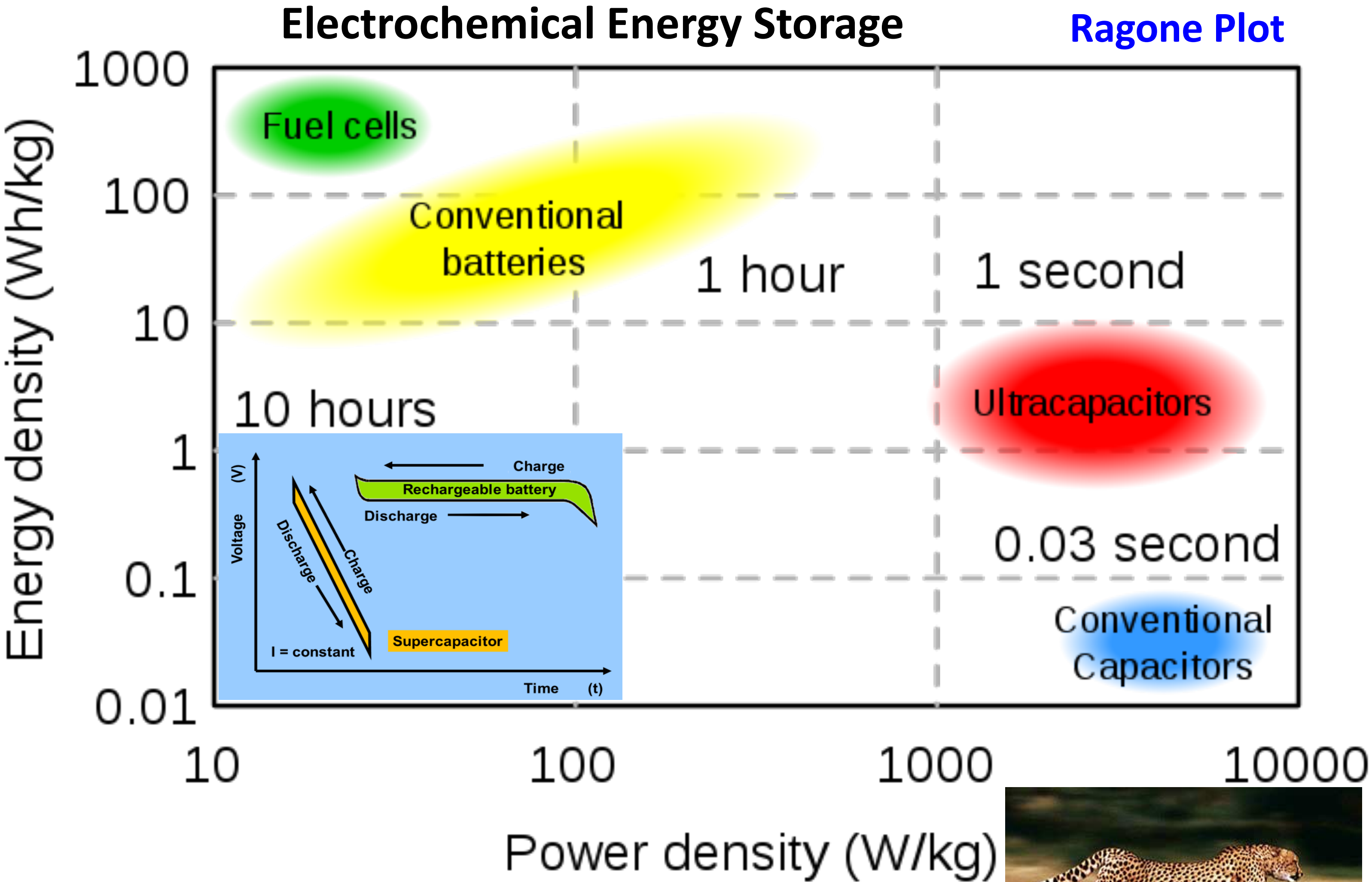
prabeer@iisc.ac.in
http//www.prabeer.org

Epicenter (M 38, Indian)

Camel/
Marriage

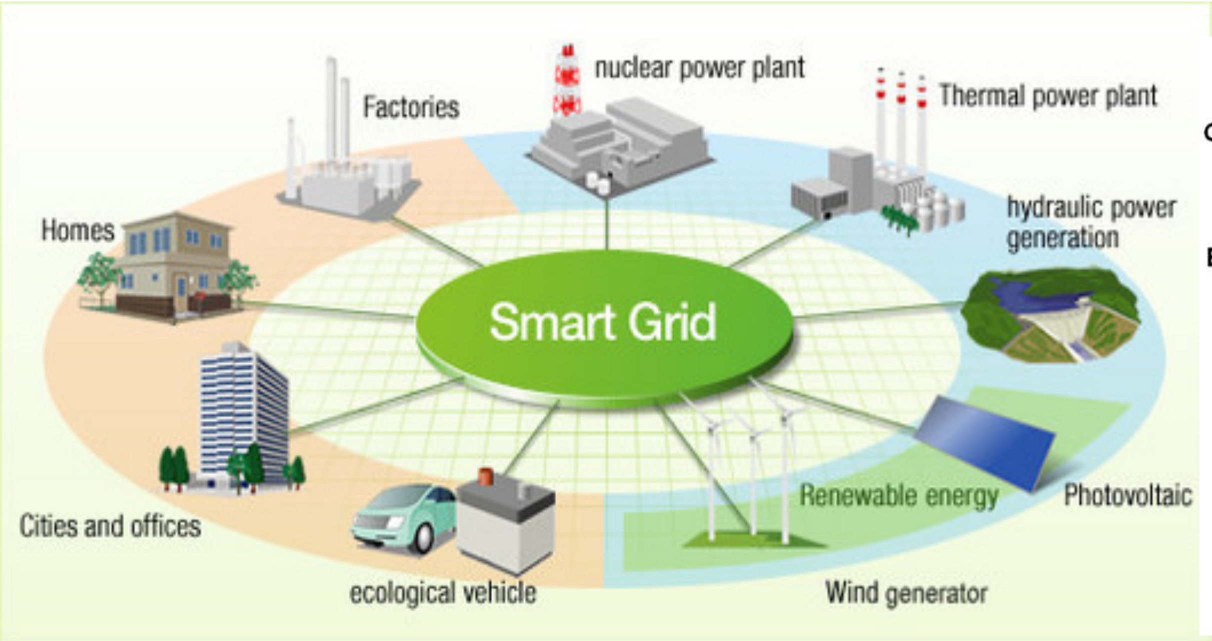


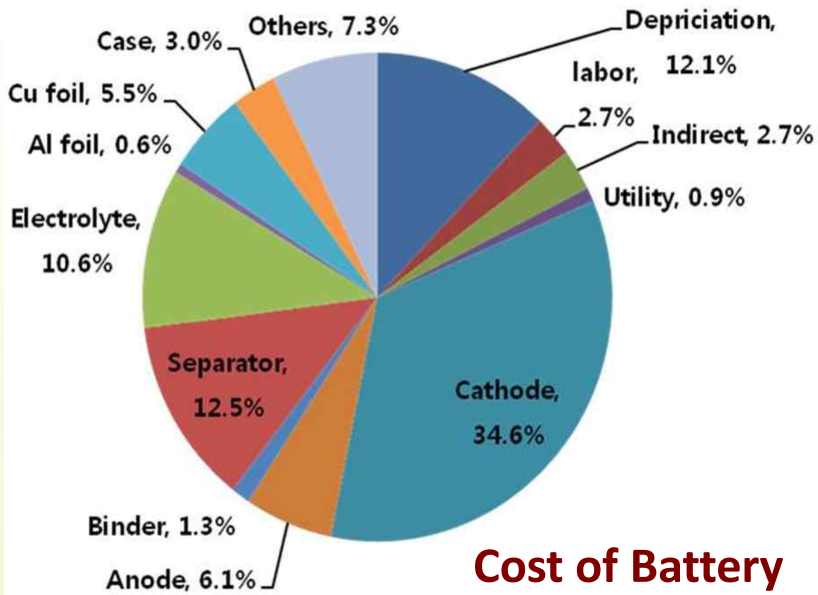
Leopard/
Dating

Electrochemical Energy Storage --------**electron**-------Electricity

Rechargeable Batteries (circa 1990 ----)

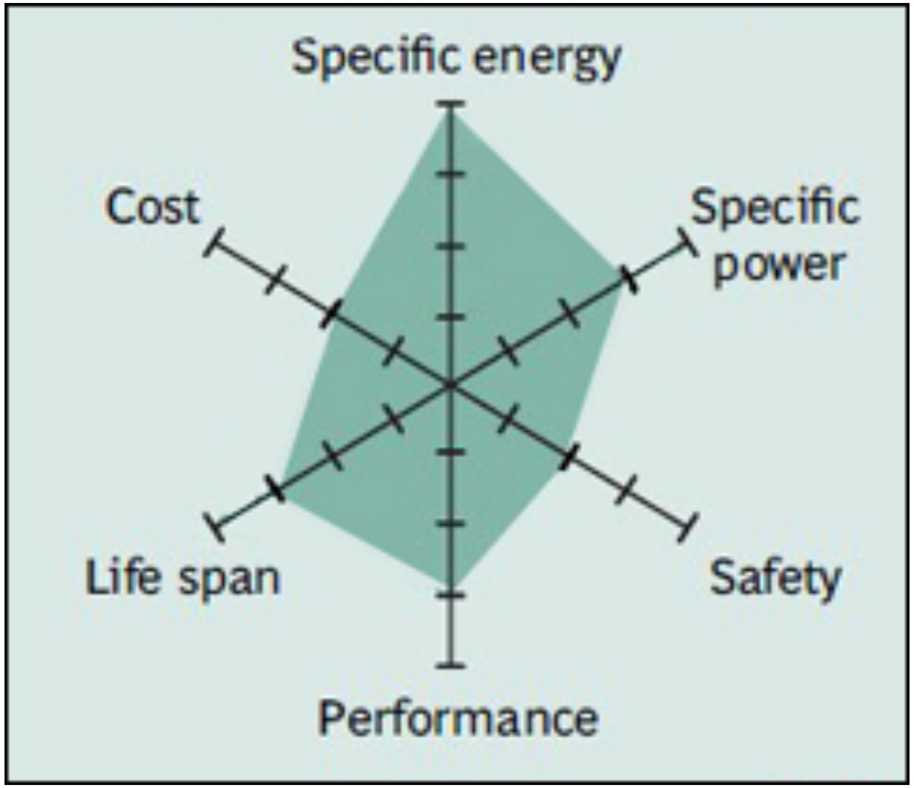
Portable Electronics → **Hybrid Vehicles** → **Grid Power Storage**





Cost of Battery

An Ideal Battery is Like an Ideal Spouse



* High Energy Density : Range of Travel (80-200 km/ charge)

* High Power Density : Fast pick-up and fast charging

* High Economy : Affordable and easy to manufacture

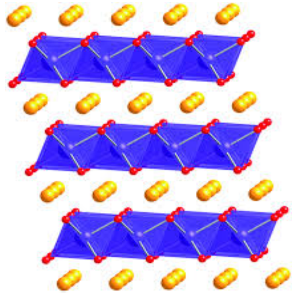
* High Safety : Safe operation and storage

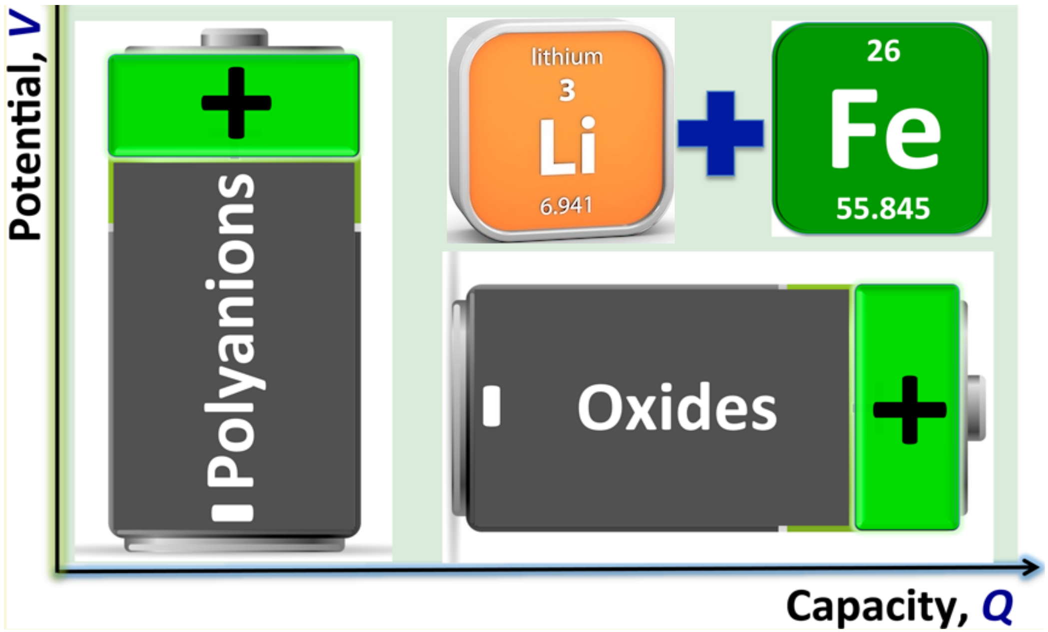
Emphasis on Cost and Safety

Energy Density = Potential (V) x Capacity (Q)

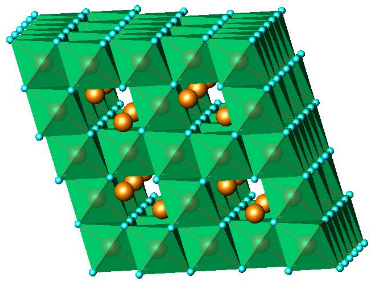
$$\text{Capacity } (Q_{Th}) = \frac{26800\ (F/3600)}{\text{Molecular Weight (Mw)}} \times n\,e^{-}$$

Li_xCoO_2

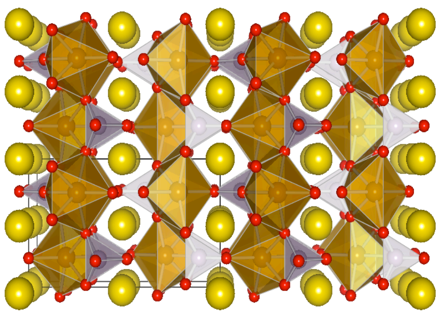




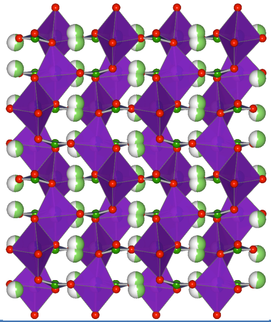
$Li_xMn_2O_4$



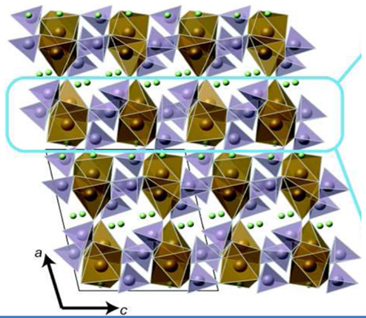
Li_xFePO_4



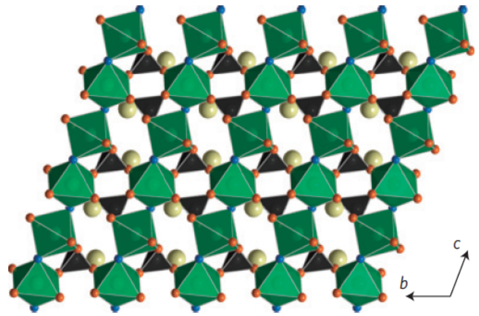
Li_xFeBO_3



$Li_{2-x}FeP_2O_7$

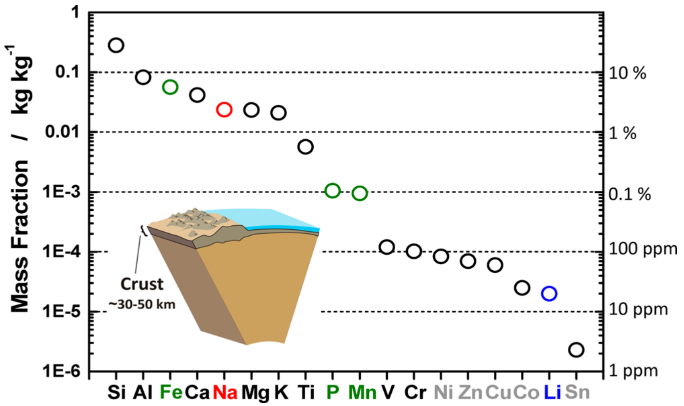


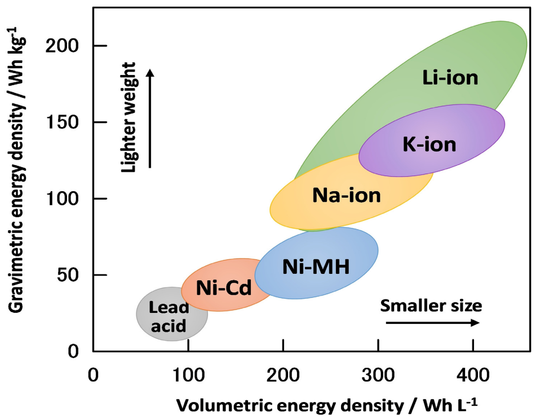
Li_xFeSO_4F

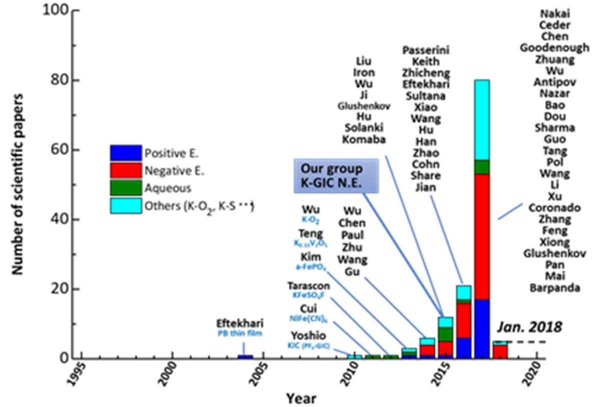


Potassium-ion Batteries

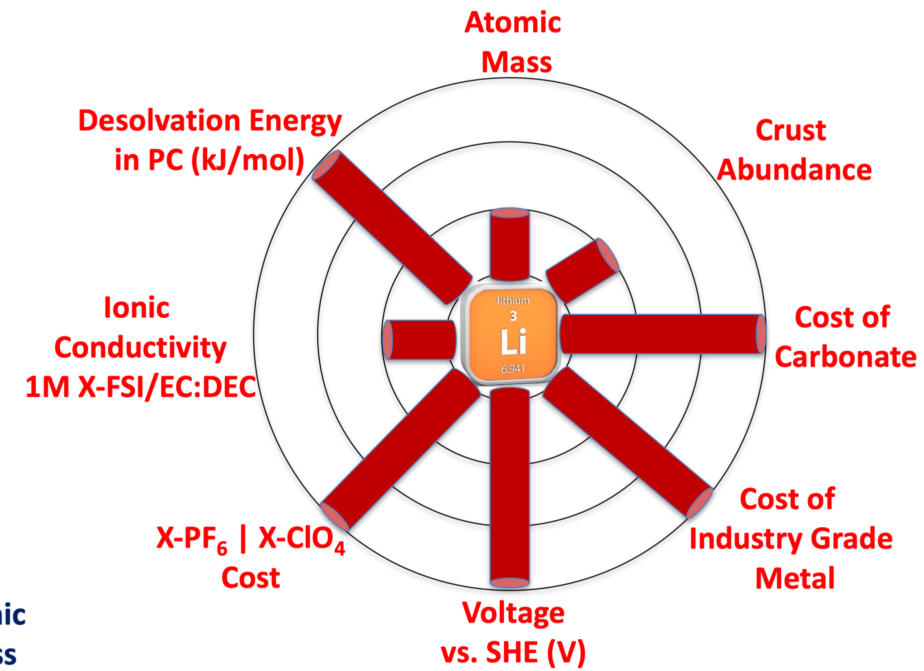
Properties	Li^+	Na^+	K^+
Elemental abundance (ppm)	20	23600	20000
Relative atomic mass:	6.94	23.0	39.10
Mass-to-electron ratio	6.94	23.0	39.10
Shannon's ionic radii (Angstrom)	0.76	1.02	1.38
E^0 (vs. SHE)/ V	-3.04	-2.71	-2.93
Melting point/ C	180.5	97.7	63.4
Theoretical capacity of $ACoO_2$ (mAh g^{-1})	274	235	----
Molar conductivity in $AClO_4$:PC (S cm^2 mol^{-1})	6.54	7.16	----
Desolvation energy in PC (kJ mol^{-1})	218.0	157.3	119.2
Coordination preference	oct/tet	oct/pris.	prismatic
Cost of carbonate (USD/ ton)	23000	200	1000

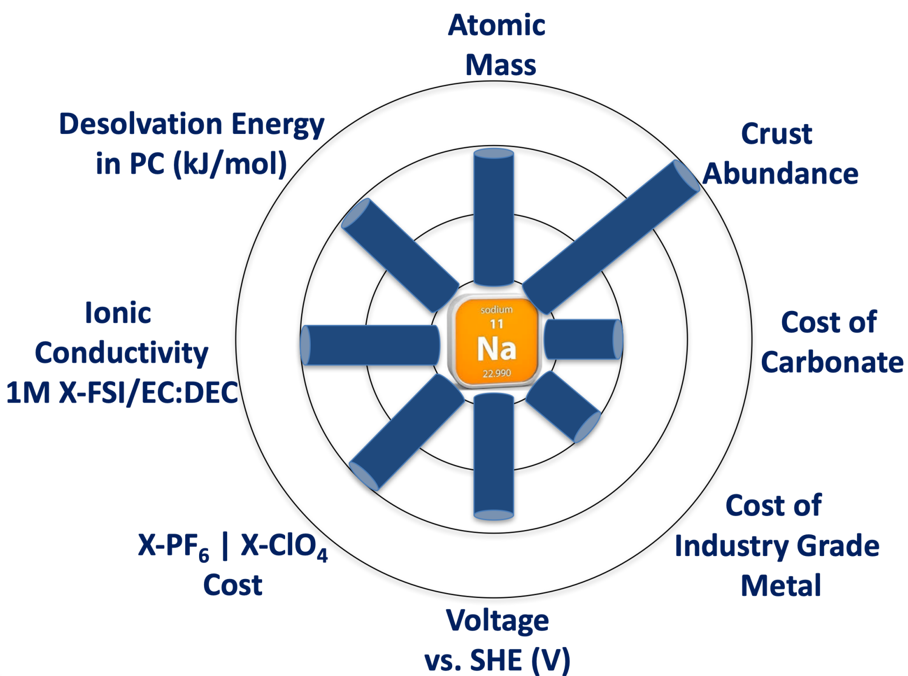


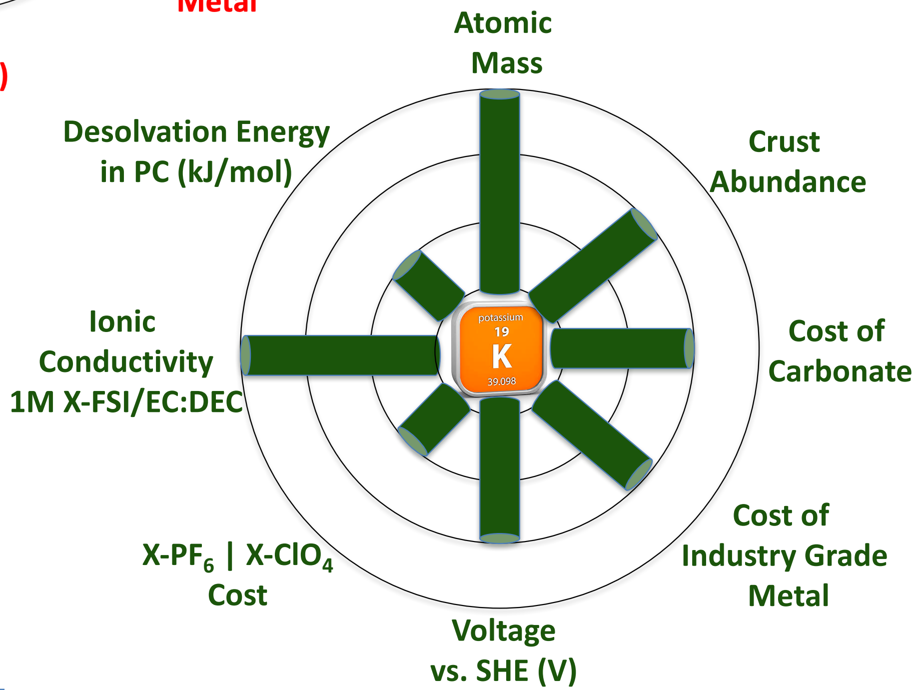




Battery Electrodes: The Alkali Ions

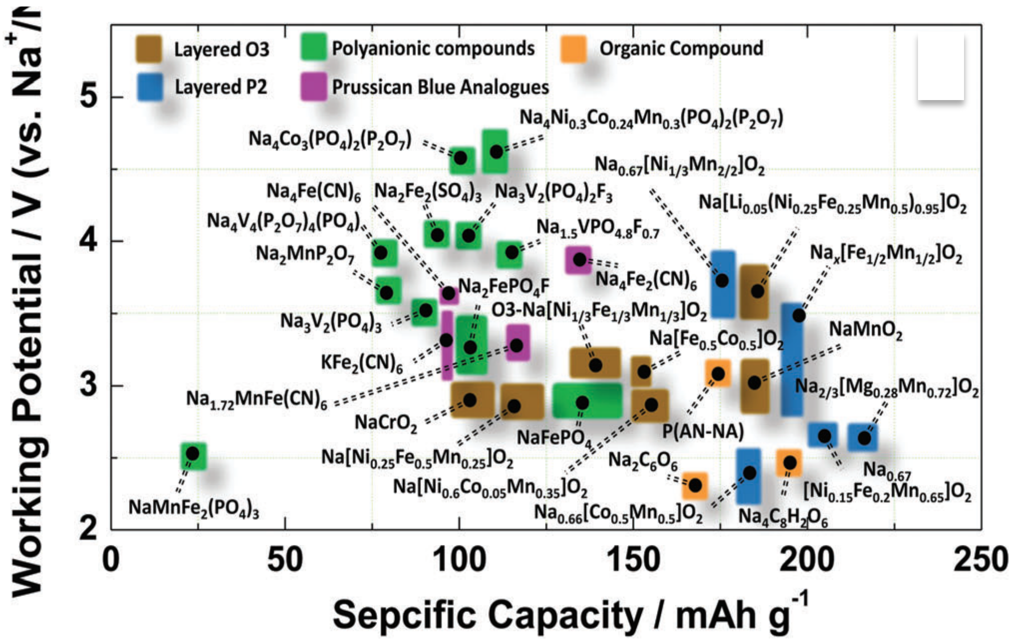






$Na_2Mn_3O_7$ = A Versatile Intercalation Host

I. $Na_2Mn_3O_7$: A 2.1 V cathode for Na-ion Batteries

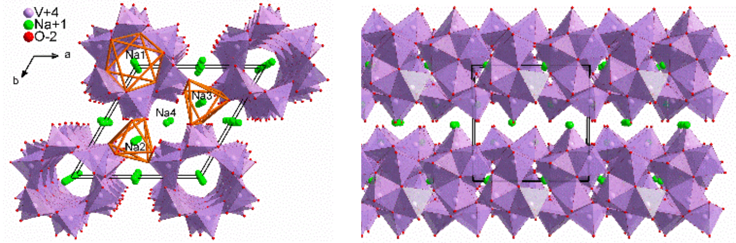


* J. Hwang, S.T. Myung, Y.K. Sun, *ChemSocRev*, 46, 3529 (2017).
* N. Yabuuchi et al, S. Komaba, *Chem. Rev.*, 114, 11636 (2014).
* P. Barpanda et al, A. Yamada, *Adv. Energy Mater.*, 8, 1703055 (2018).

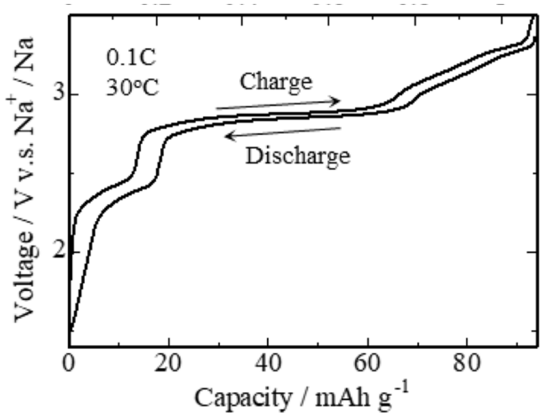
Overview of $Na_2M_3O_7$ (M = 3d metals) Class of Electrodes

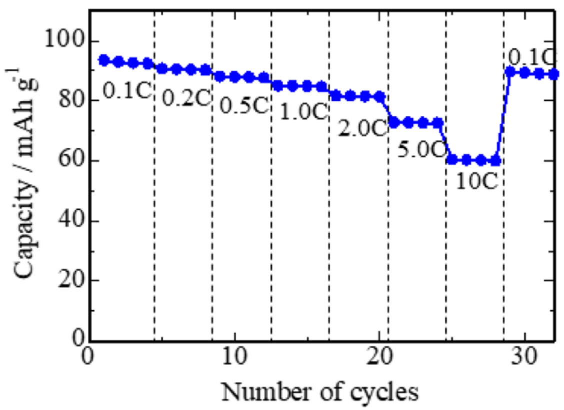
(+) $Na_2V_3O_7$

$Na_2O + 3\ VO_2$ ---- (600 C/ 12h/ vacuum) ------ **$Na_2V_3O_7$**



* $Na_2V^{IV}_3O_7$ ~ trigonal (*P*31*c*)
* $Na_2V^{IV}_3O_7$ - 2 Na ---- $NaV^{V}_3O_7$
* Lowest redox potential (0.3 V) anode

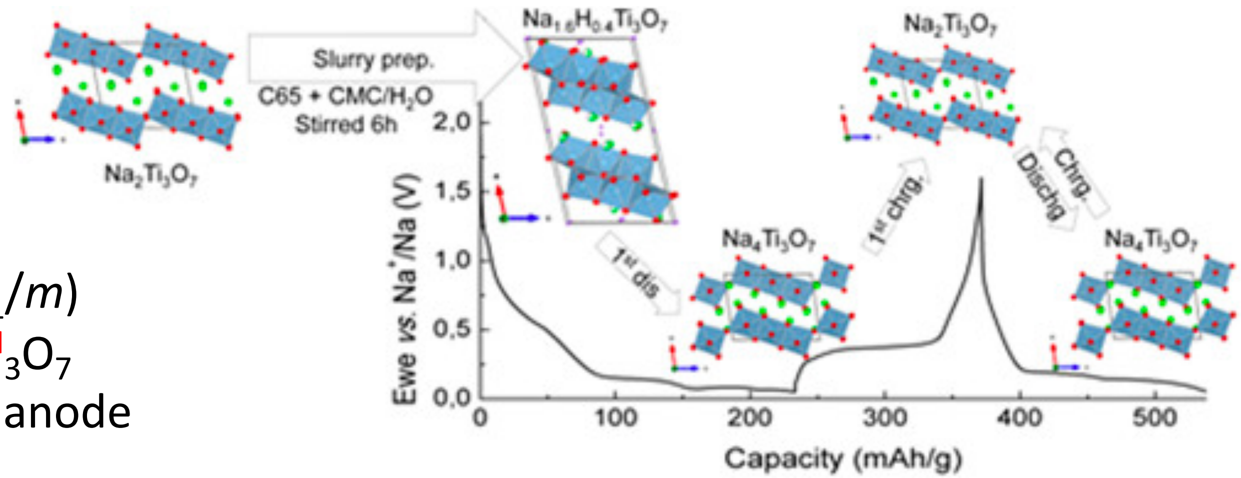




(-) $Na_2Ti_3O_7$

$Na_2CO_3 + 3\ TiO_2$ ---- (800 C/ 40h) ------ **$Na_2Ti_3O_7$**

* $Na_2Ti^{IV}_3O_7$ ~ Monoclinic ($P2_1/m$)
* $Na_2Ti^{IV}_3O_7$ + 2 Na ---- $Na_4Ti^{III}_3O_7$
* Lowest redox potential (0.3 V) anode

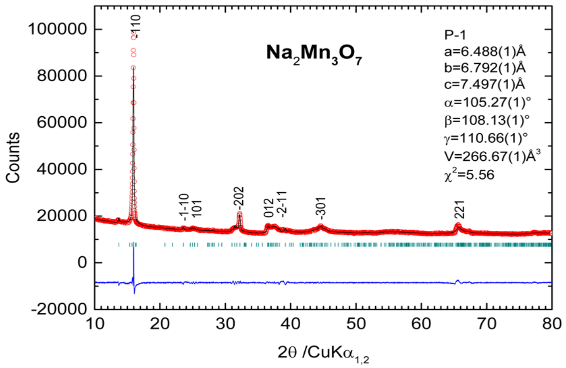


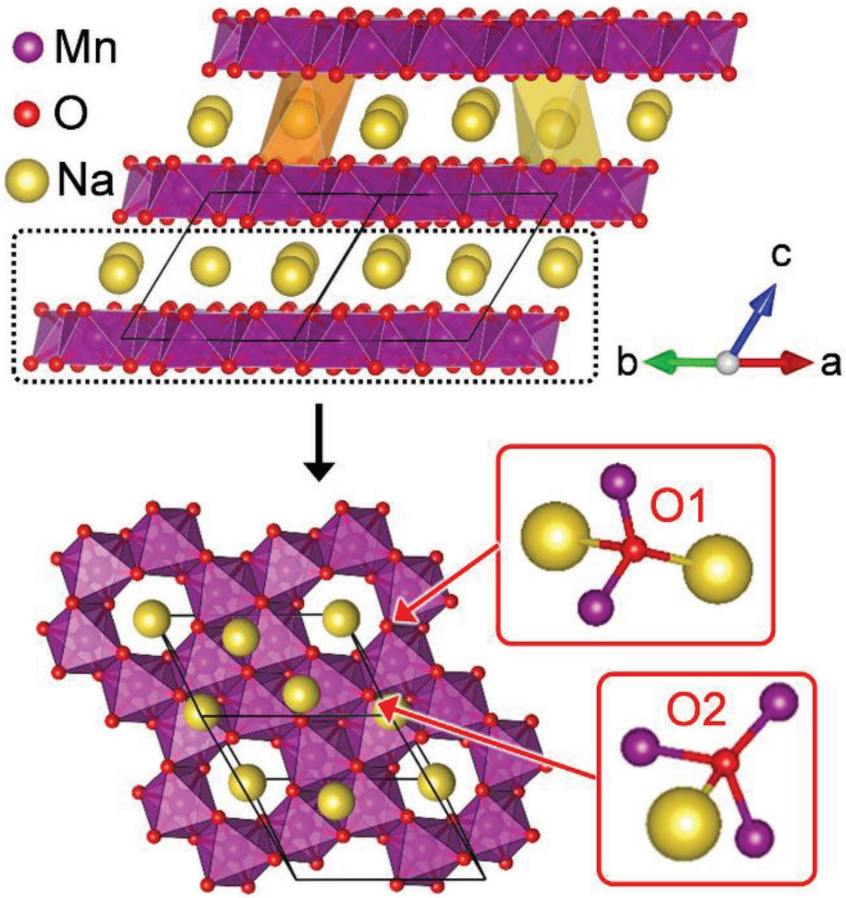
* N. Tanibata et al, S. Okada, *Sci. Rep.*, 8, 17199 (2018).
* E. Adamczyk et al, V. Pralong, *Materials*, 11, 1021 (2018).
* P. Senguttuvan et al, J.M. Tarascon, M.R. Palacin, *Chem. Mater.*, 23, 4109 (2013).

$Na_2Mn_3O_7$ as a 2.1 V Sodium Insertion Material

2 $NaNO_3$ + 3 $MnCO_3$ + O_2 ------- (600 C/ 4h) ------ **$Na_2Mn_3O_7$** + 2 NO_2 + 3 CO_2

Triclinic (*P*-1) Crystal Structure



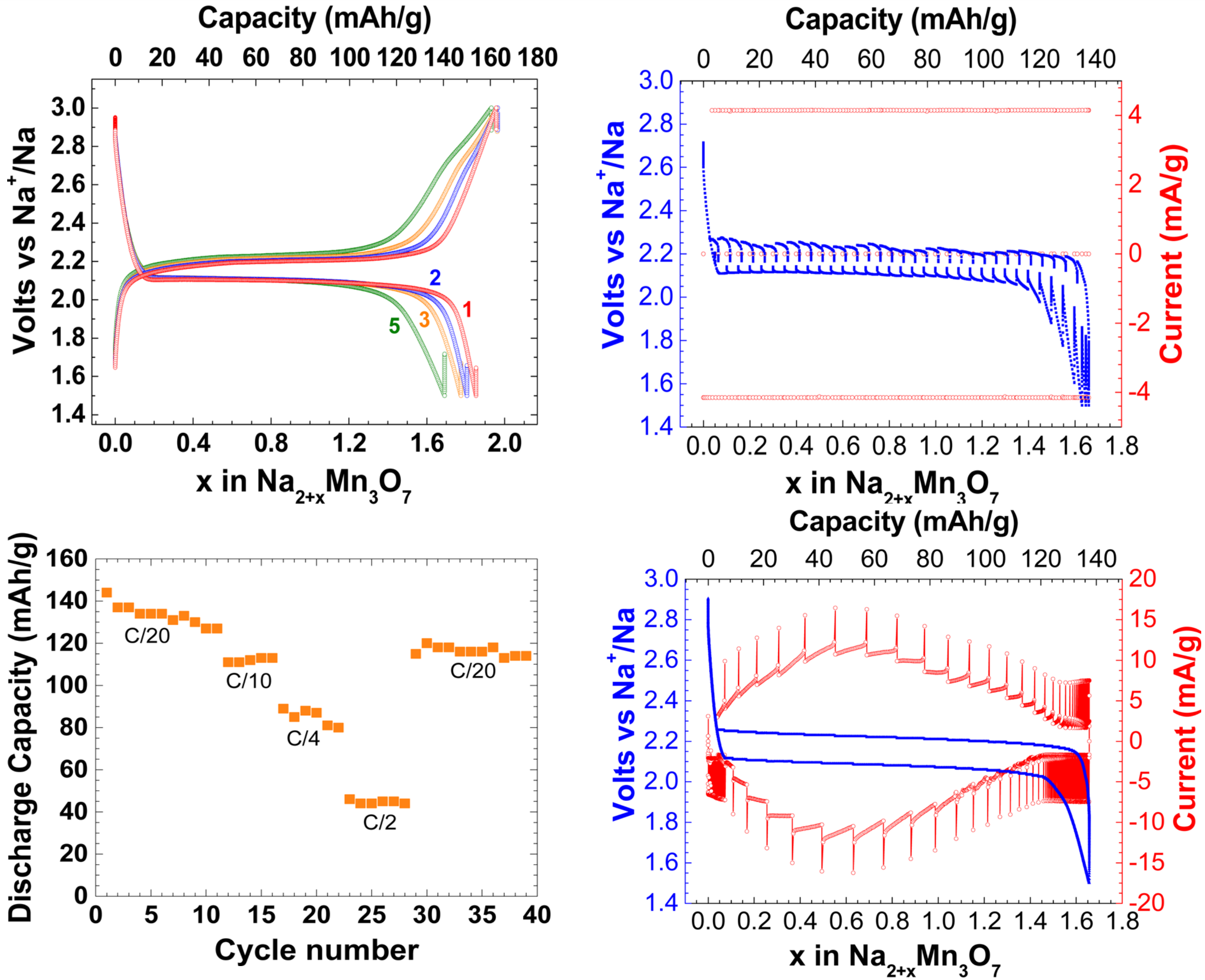


* Triclinic (P-1) Layered Structure Material
* Non-toxic, Easy to Synthesize, Scalable, Economic

* F.M. Chang, M. Jansen, *Z. Anorg. Allg. Chem.*, 531, 177-182 (1985).
* E. Adamczyk, V. Pralong, *Chem. Mater.*, 29, 4645-4648 (2017).

$Na_2Mn_3O_7$ as a 2.1 V Sodium Insertion Material

Electrochemical Analyses

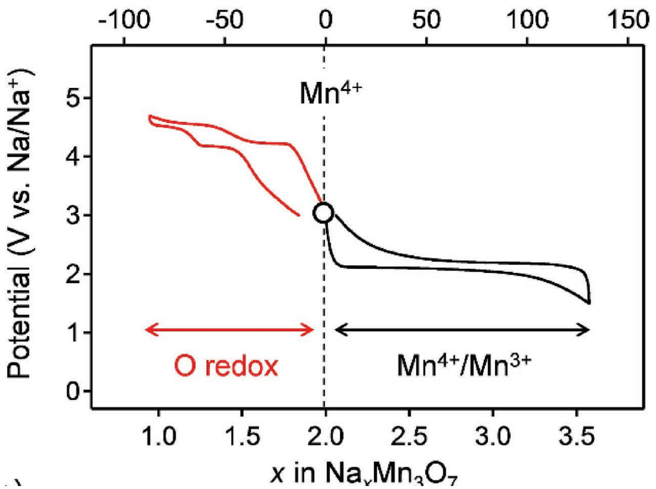


* $Na_2Mn_3O_7$ as a 2.1 V Cathode. * Biphasic redox reaction. * Energy density ~ 336 Wh/kg

$Na_4Mn_3O_7$ ~ rock salt structure?

* E. Adamczyk, V. Pralong, *Chem. Mater.*, 29, 4645-4648 (2017).

II. $Na_2Mn_3O_7$: A 4.1 V Anionic Redox Cathode



Anionic Redox : A New Paradigm in Battery

RESEARCH ACCOUNT

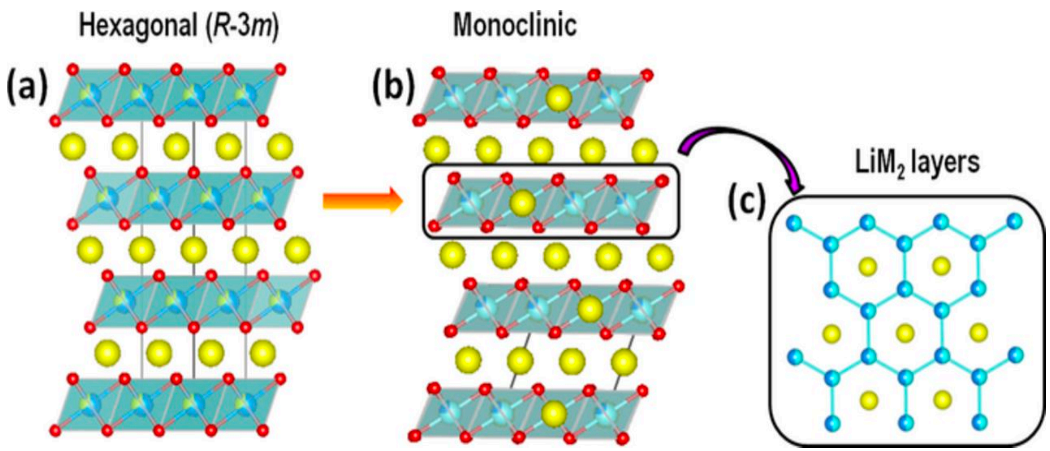
Some solid state chemistry with holes: Anion–cation redox competition in solids*

Jean Rouxel

Collège de France, 11 Place Marcelin Berthelot, 75231 Paris Cedex 5, France and
Institut des Matériaux de Nantes, UMR 6502, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France

Prof. Jean Rouxel
(1935-1998, FRA)

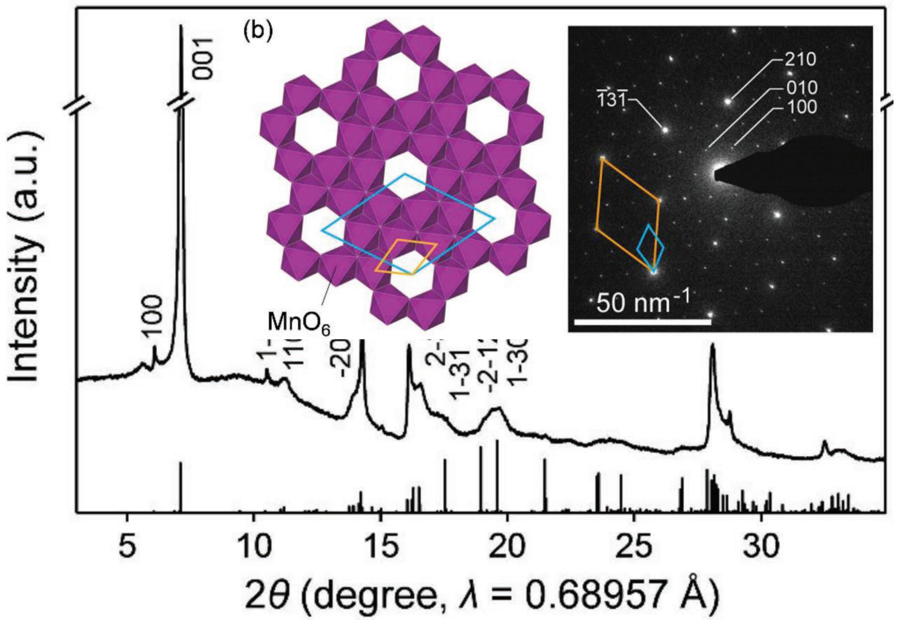
1. (extra) Li|Na in MO_6 layers



Conventional Layered Oxides

Li/Na-rich Layered Oxides

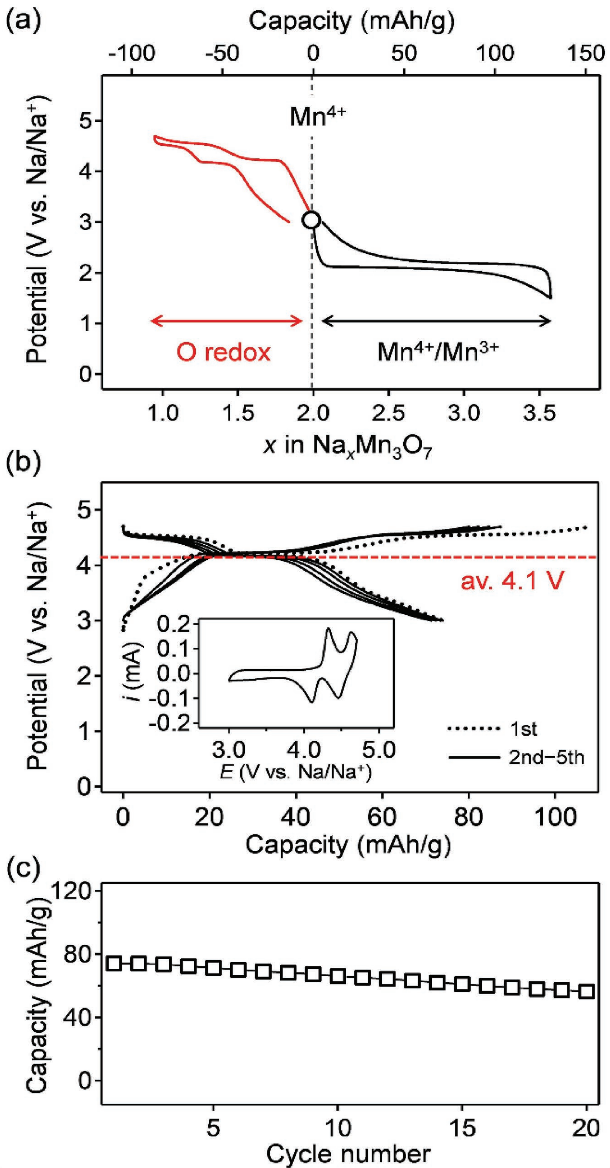
2. Vacancy in MO_6 layers



* J. Rouxel, *Curr. Sci.*, 73, 31 (1997).
* M. Sathiya et al, J.M. Tarascon, *Nat. Mater.*, 12, 827 (2013).

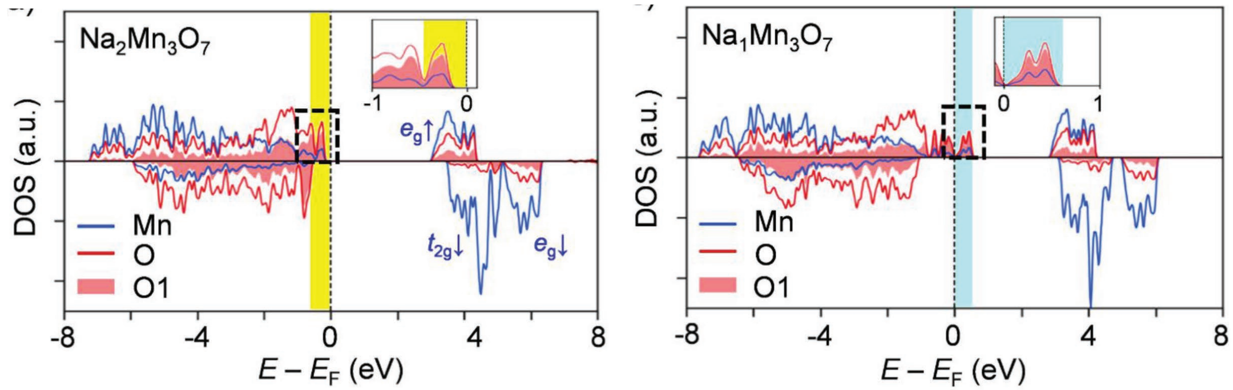
4.1 V Anionic Redox Activity in $Na_2Mn_3O_7$

Galvanostatic Cycling

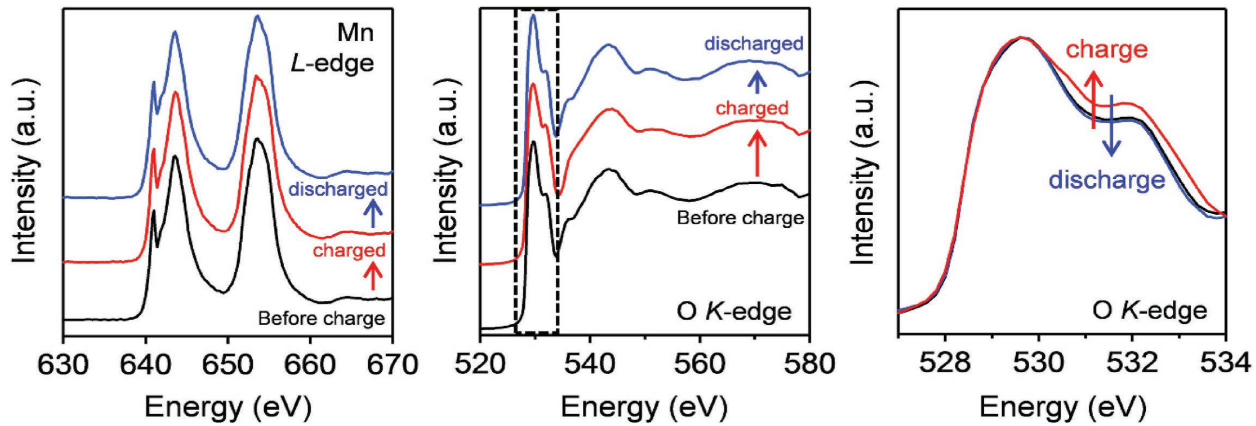


$Na_2Mn_3O_7$ ~ $Na_{4/7}[\square_{1/7}Mn^{4+}_{6/7}]O_2$

Ab-initio (DFT) Calculations



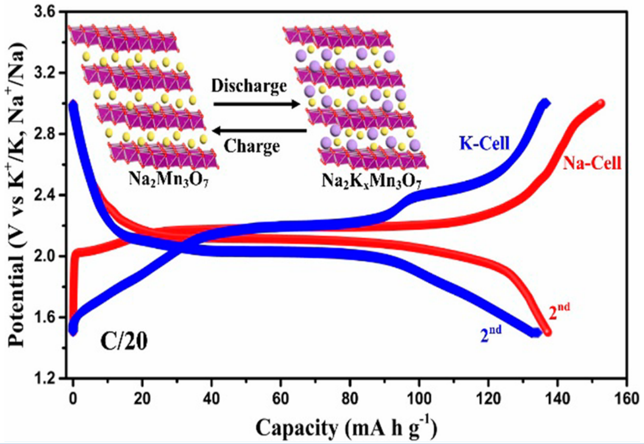
X-ray Absorption Spectroscopy



$Na_2Mn_3O_7$: 2.1 V cationic Redox + 4.1 V anionic redox activity

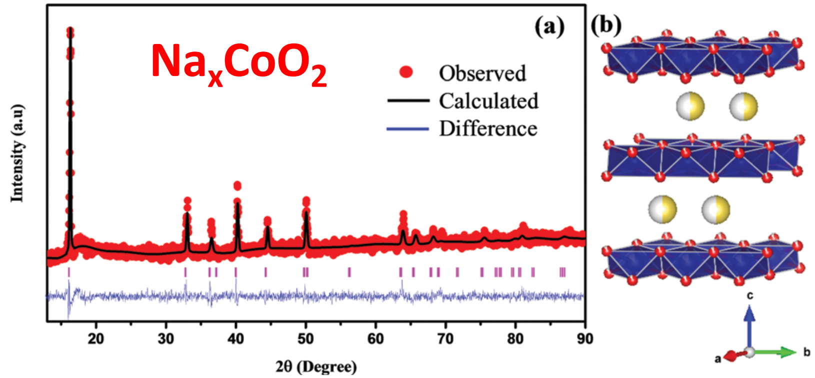
* B. M. De Boisse et al, A. Yamada, *Adv. Energy Mater.*, 8, 1800409 (2018).

III. $Na_2Mn_3O_7$: A 2.1 V Potassium Insertion Material



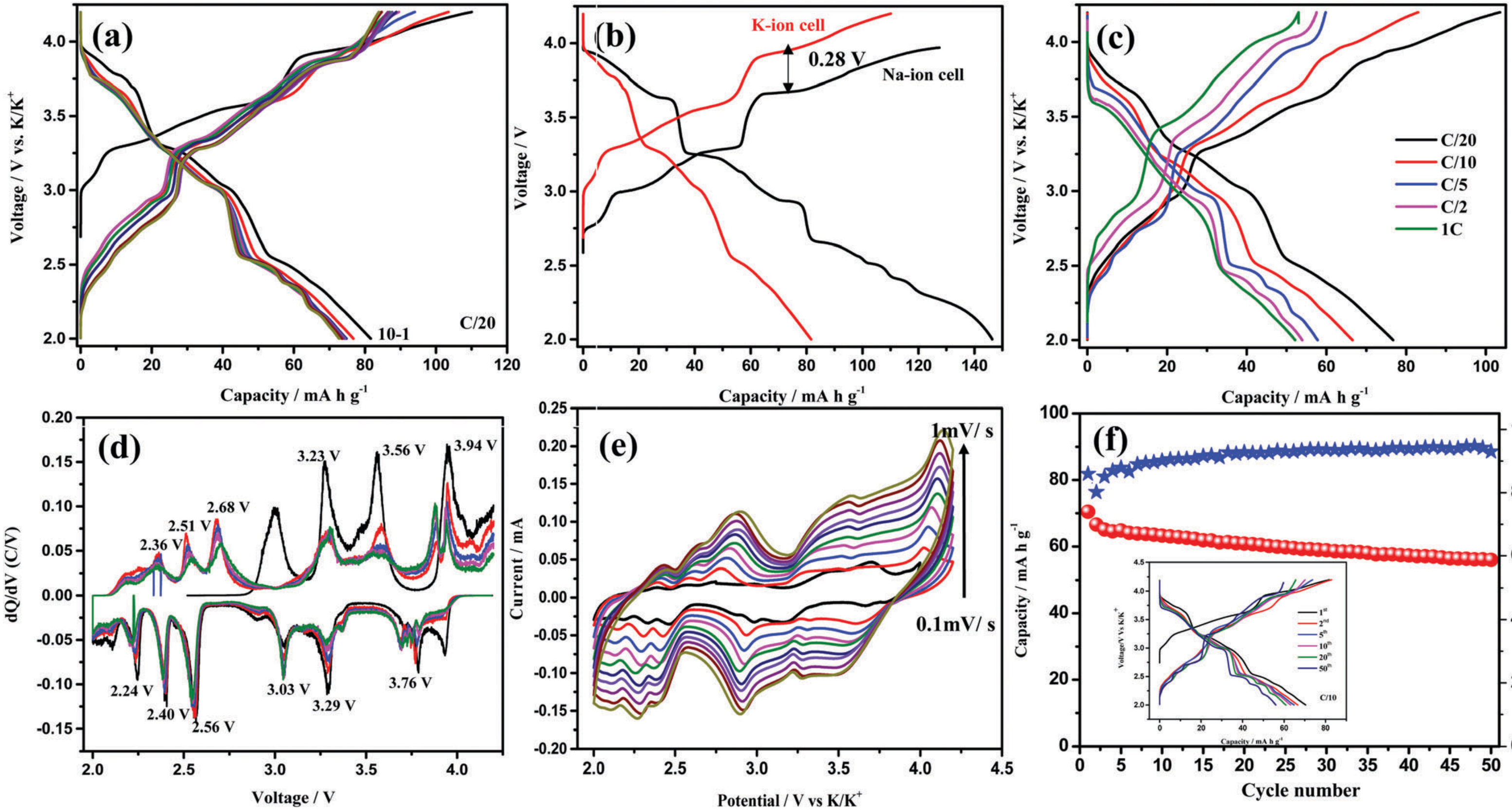
* K. Sada, B. Senthilkumar, P. Barpanda, *ACS Appl. Energy Mater.*, 1, 5410-5416 (2018).

Case 1: Na-based compounds for K insertion (Oxides)



$Na_xCo^{III}O_2 + K^+$ --------- $Na_xK_yCo^{III/IV}O_2$

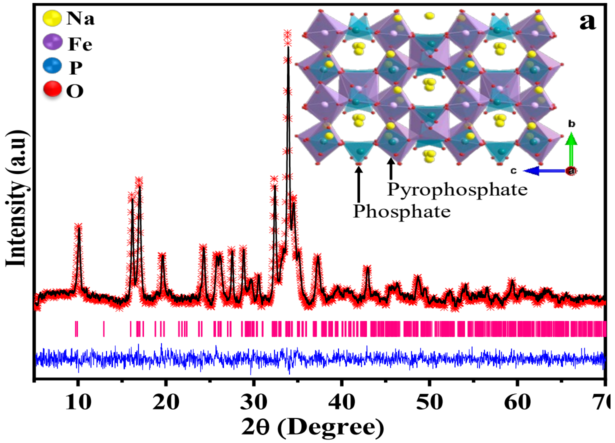
Electrochemical Analyses

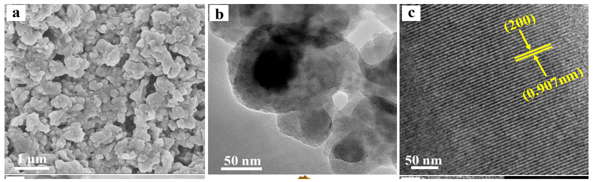


* K. Sada, B. Senthilkumar, P. Barpanda, *Chem. Commun.*, 53, 8588-8591 (2017).

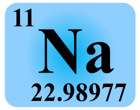
Case 2: Na-based compounds for K insertion (Polyanions)

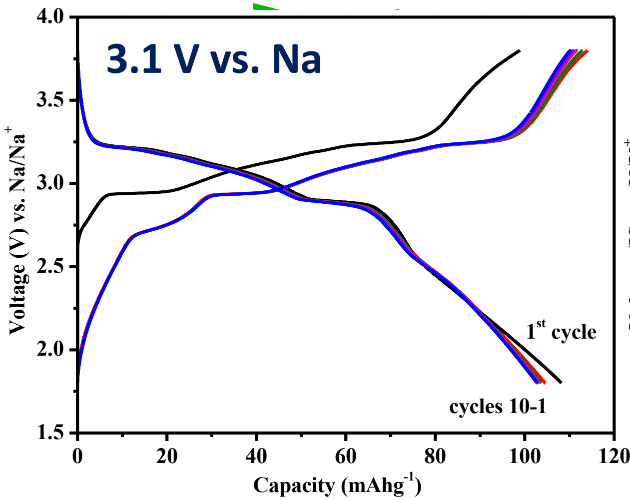
$Na_4Fe_3(PO_4)_2P_2O_7$

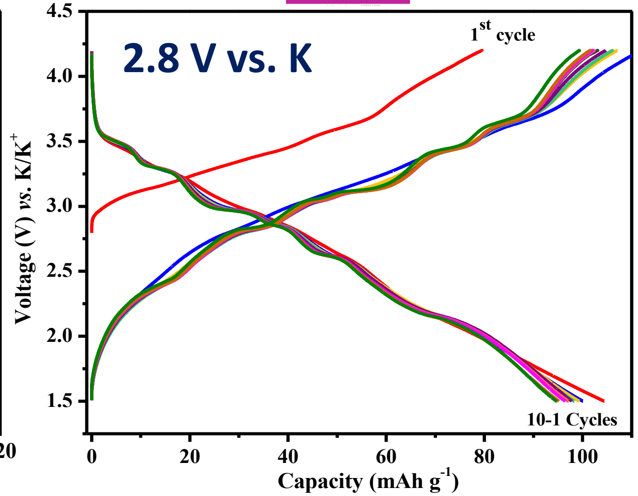




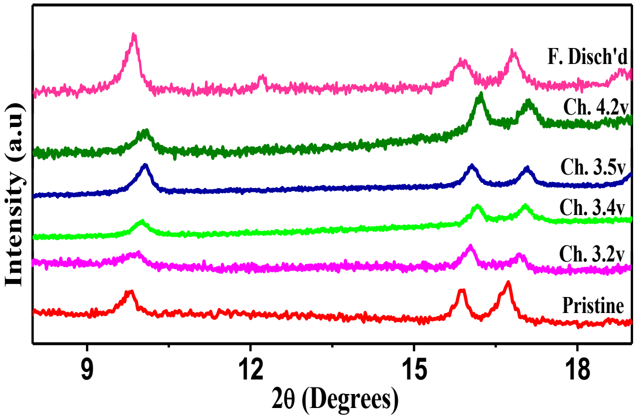
$Na_4Fe_3^{II}(PO_4)_2P_2O_7 + K^+$ ----- $NaK_3Fe_3^{III}(PO_4)_2P_2O_7$

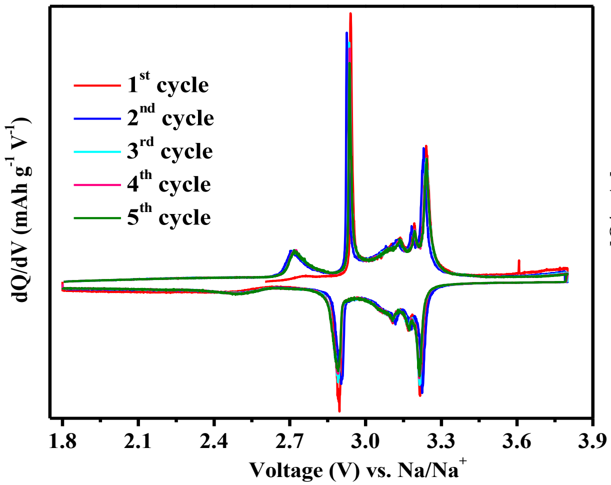


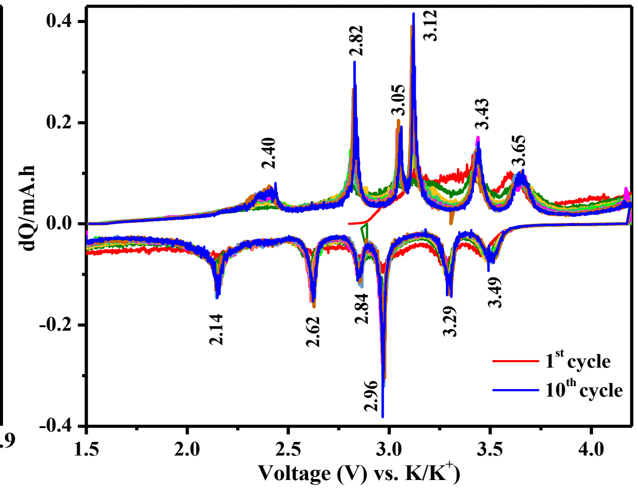




Solid-solution Redox Activity



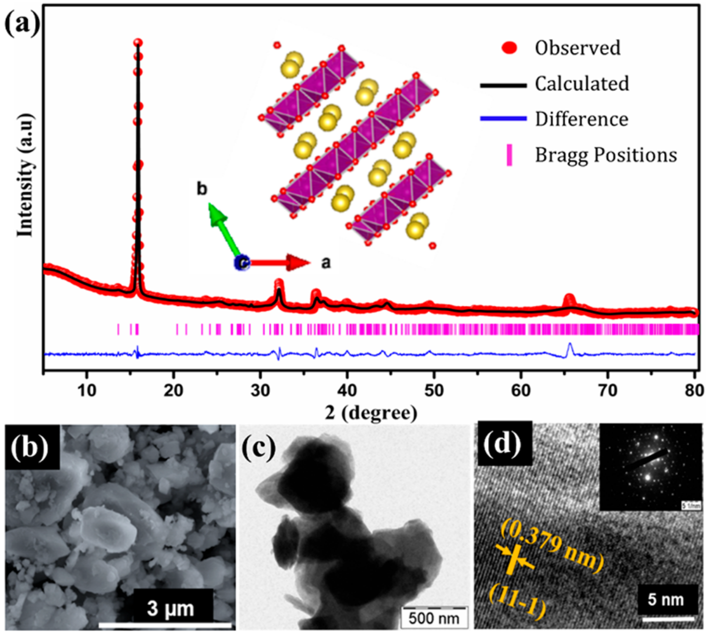


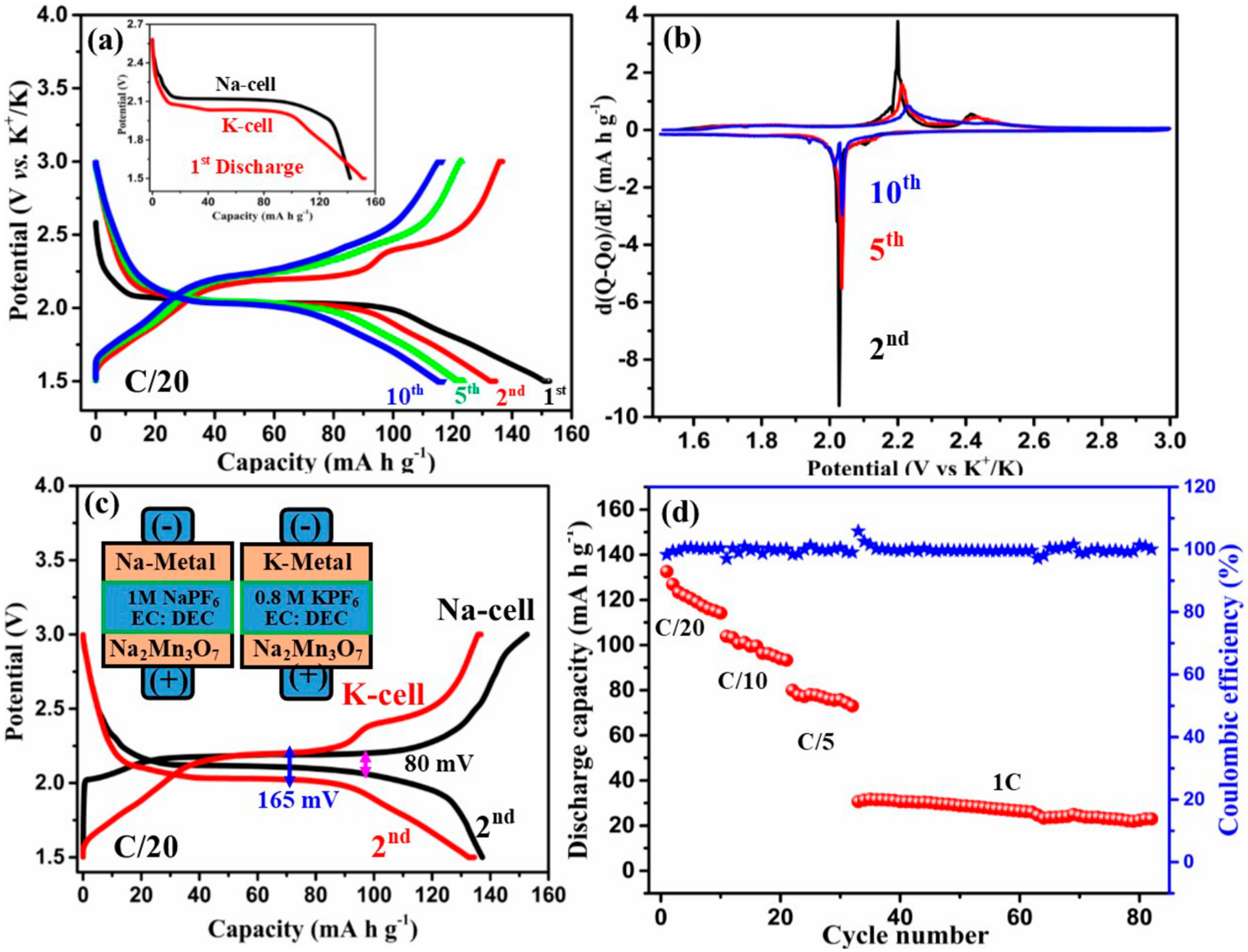


* K. Sada, B. Senthilkumar, P. Barpanda, *Chem. Commun.*, 53, 8588-8591 (2017).

K insertion into $Na_2Mn_3O_7$ layered oxide

$Na_2Mn_3O_7$ | K Architecture

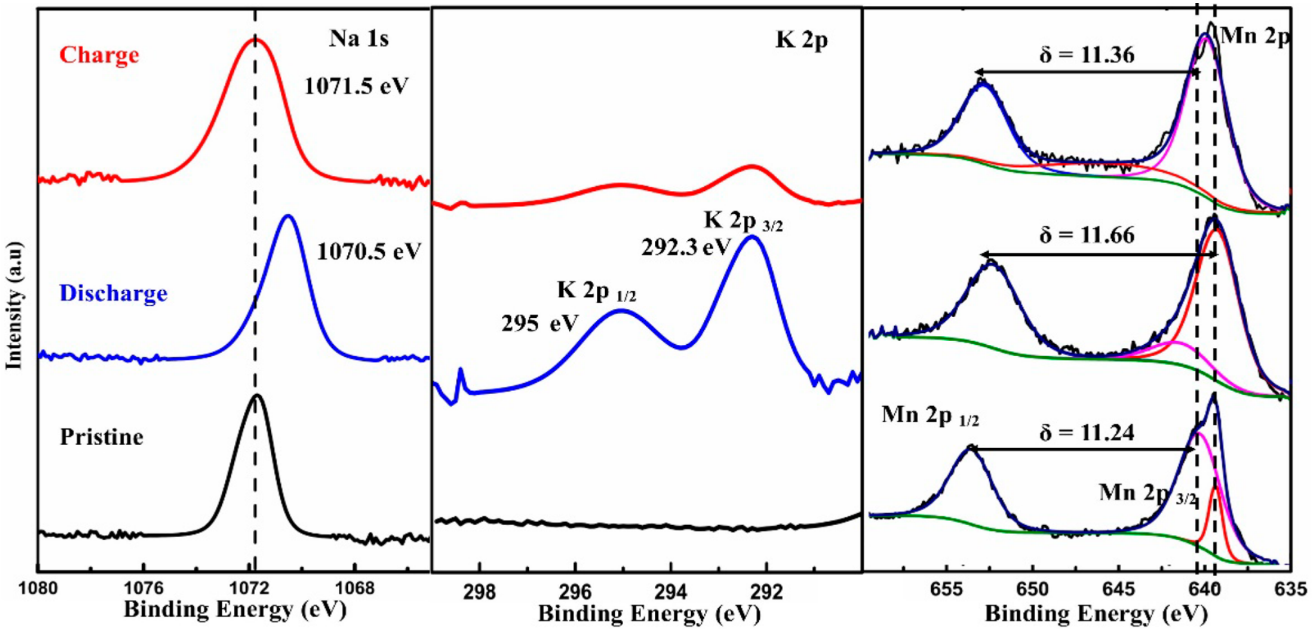




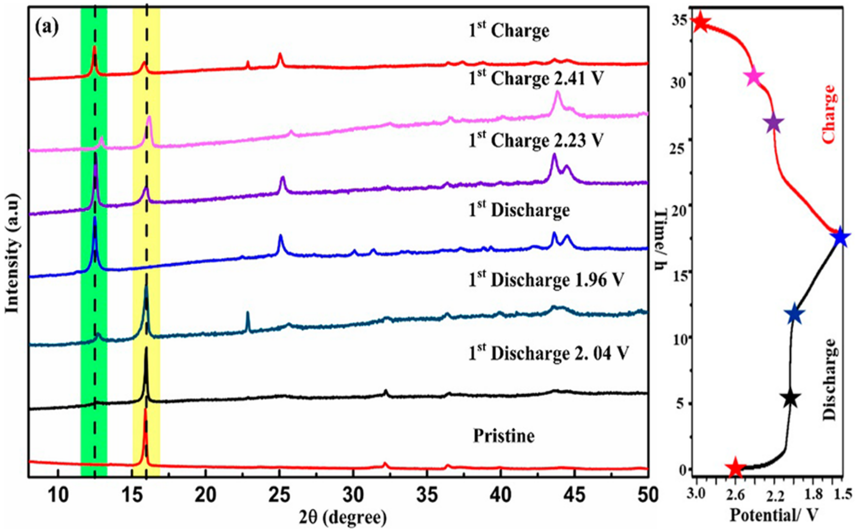
* $Na_2Mn_3O_7$: A layered structure triclinic compound
* In Potassium half-cell, it delivers ~2.1 Mn^{4+}/Mn^{3+} redox activity
* Similar to Na half-cell, it undergoes a biphasic redox activity.

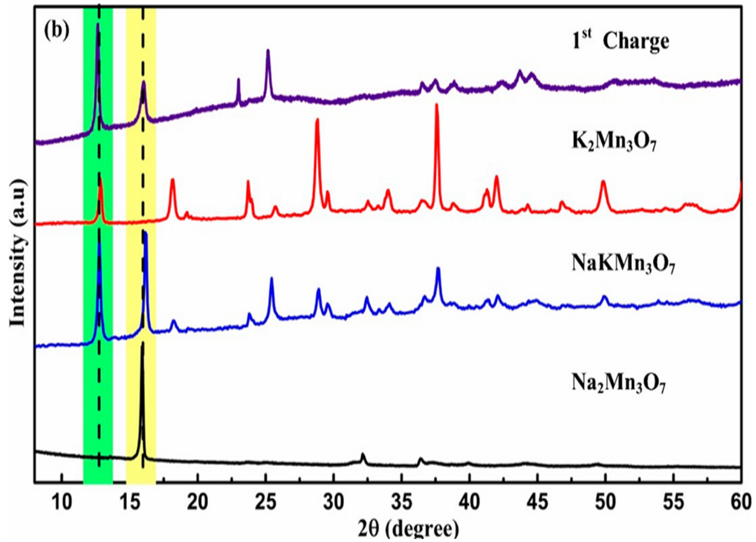
K insertion into $Na_2Mn_3O_7$ layered oxide

Ex-situ XPS Study



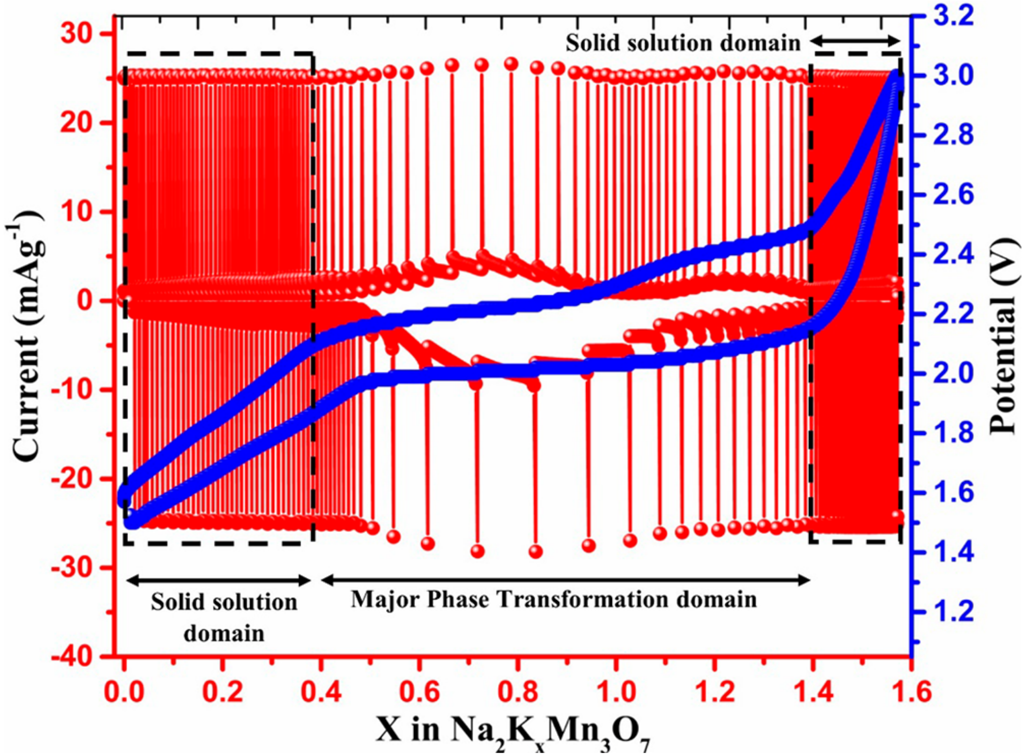
Ex-situ XRD Study

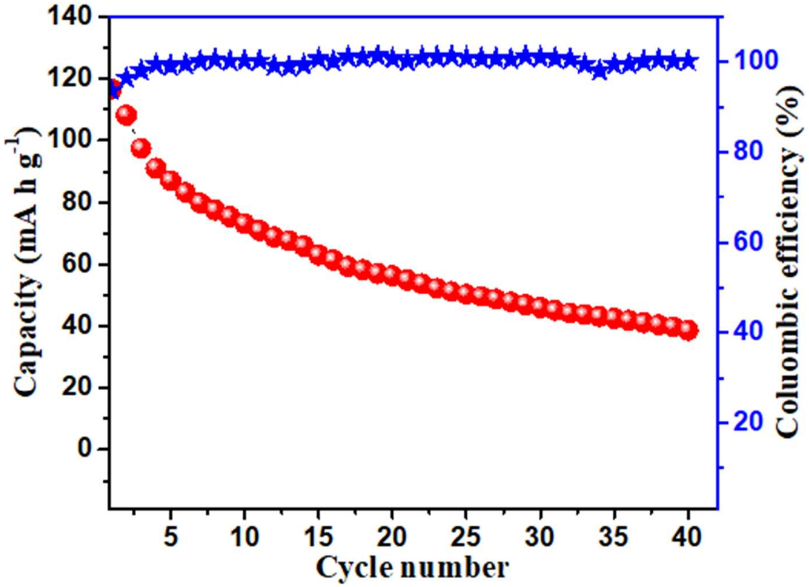




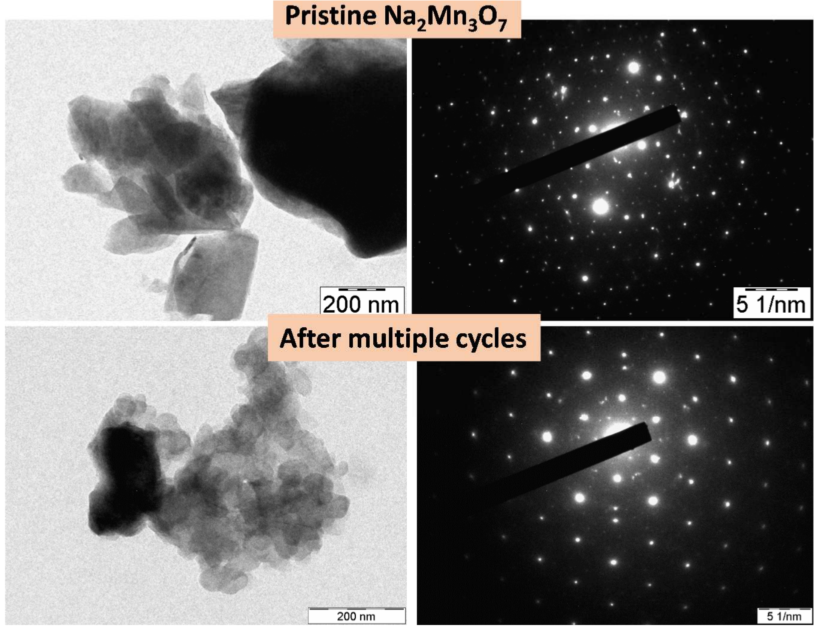
K insertion into $Na_2Mn_3O_7$ layered oxide

GITT Titration





Pristine $Na_2Mn_3O_7$

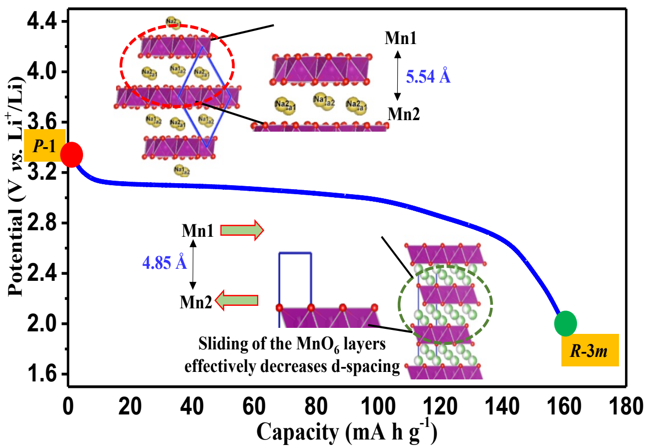


After multiple cycles

* $Na_2Mn_3O_7$ undergoes two-phase redox activity
* $Na_2Mn_3O_7$ | K cell has poor cycling stability similar to $Na_2Mn_3O_7$ | Na cell
* Structural stability is retained.

$Na_2Mn_3O_7$ work as a 2.1 V potassium-insertion host material

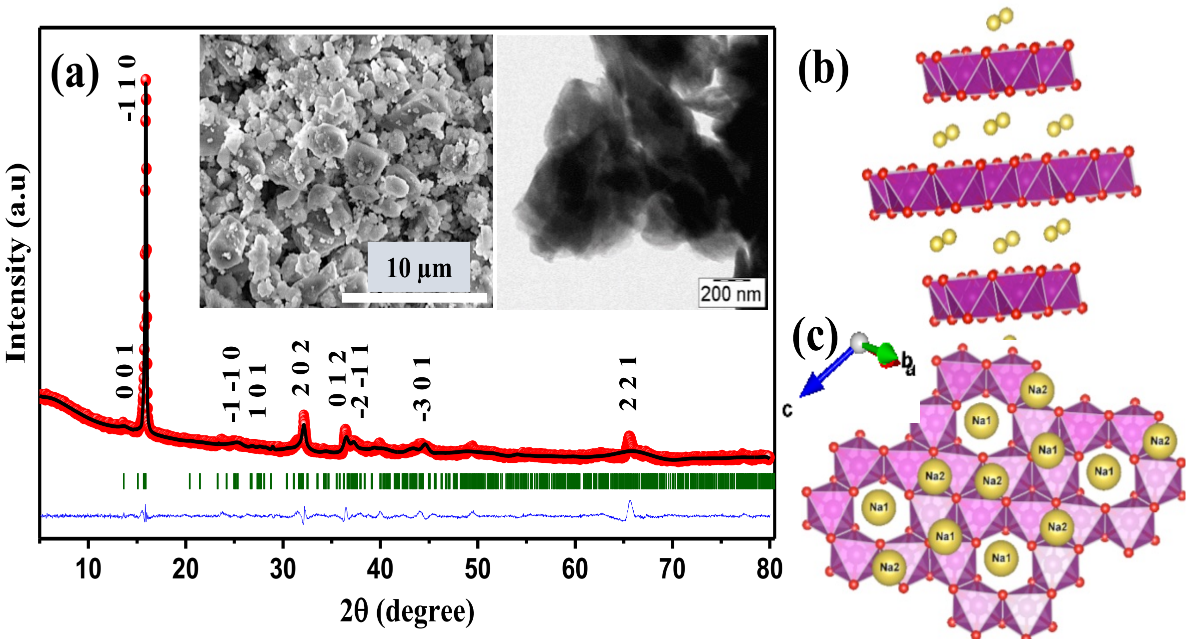
IV. $Na_2Mn_3O_7$: A 3.1 V Lithium Insertion Material

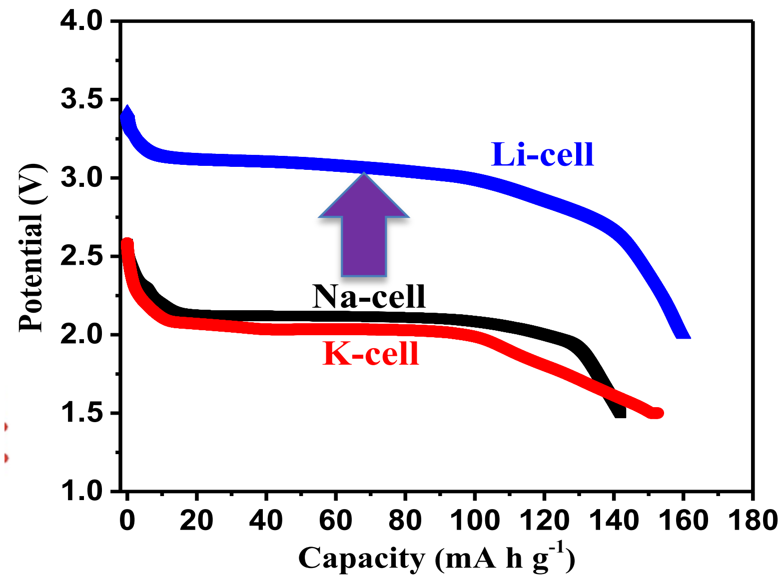


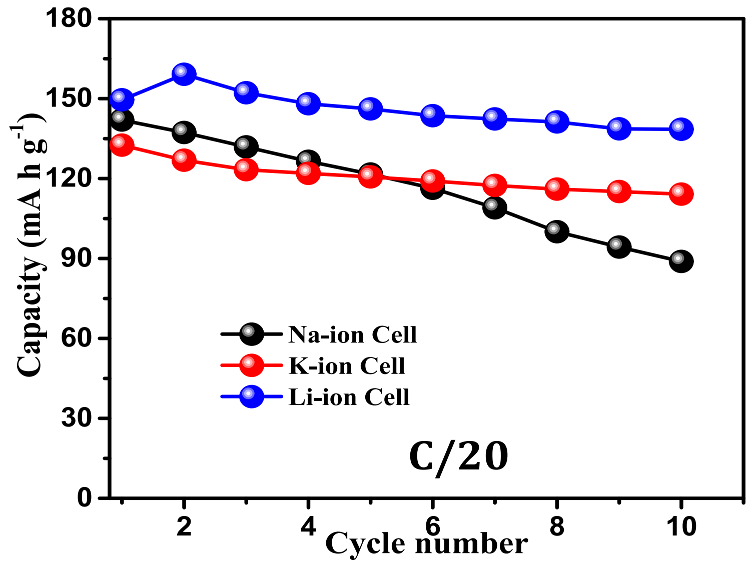
* K. Sada, B. Senthilkumar, P. Barpanda, *ACS Appl. Energy Mater.*, 1, 6719-6724 (2018).

Li insertion into $Na_2Mn_3O_7$ layered oxide

$Na_2Mn_3O_7$ | Li Architecture



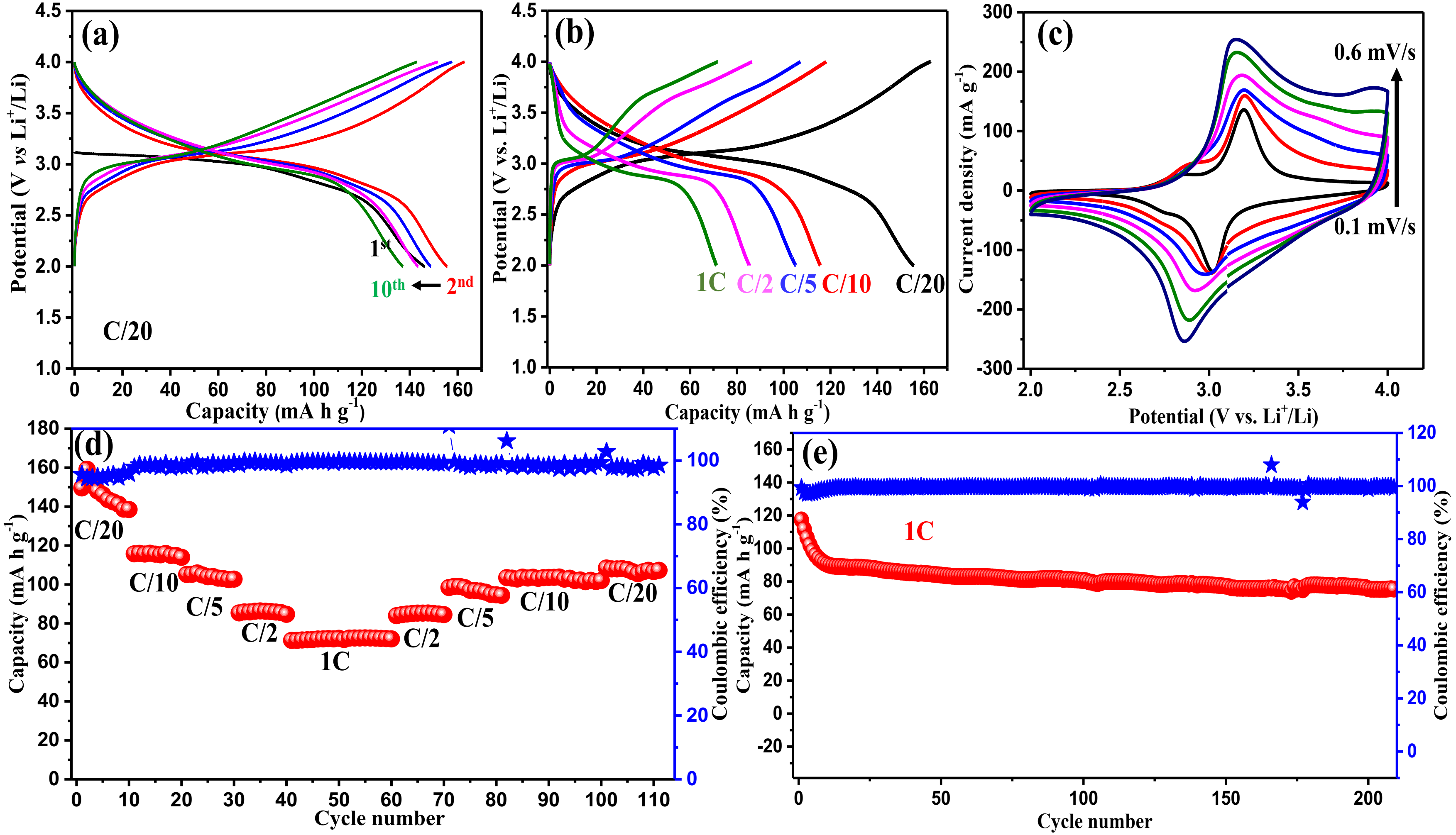




* $Na_2Mn_3O_7$ works as a 3.1 V Li-insertion material
* ~ 1 V upshift in Mn^{4+}/Mn^{3+} redox potential (similar upshift reported for $Na_2Ti_3O_7$ vs $Li_2Ti_3O_7$)
* $Na_2Mn_3O_7$ | Li cell has superior cycling stability when compared to $Na_2Mn_3O_7$ | (Na/K) cells
* Structural stability is retained.

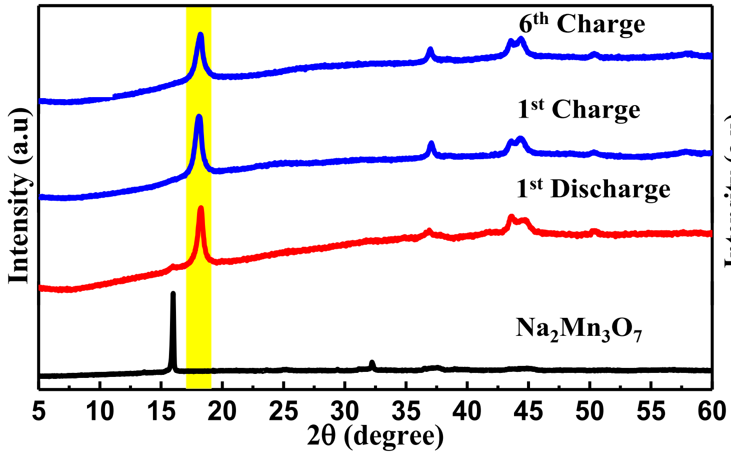
Li insertion into $Na_2Mn_3O_7$ layered oxide

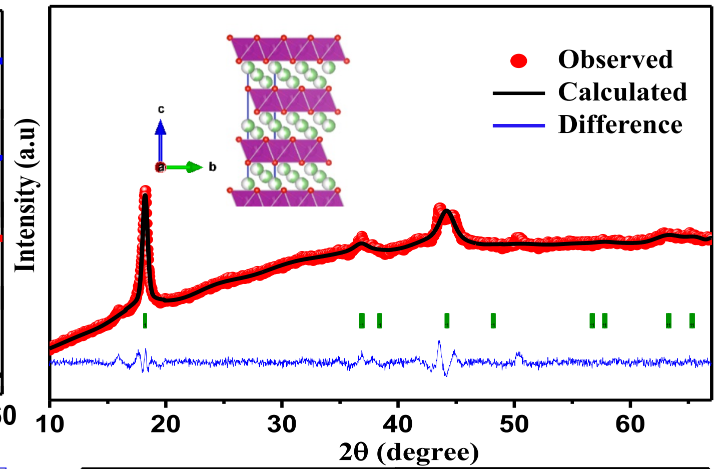
Galvanostatic Charge-Discharge

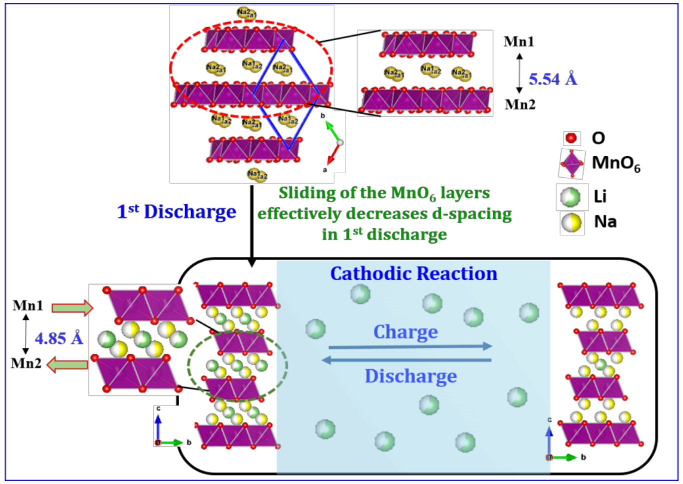


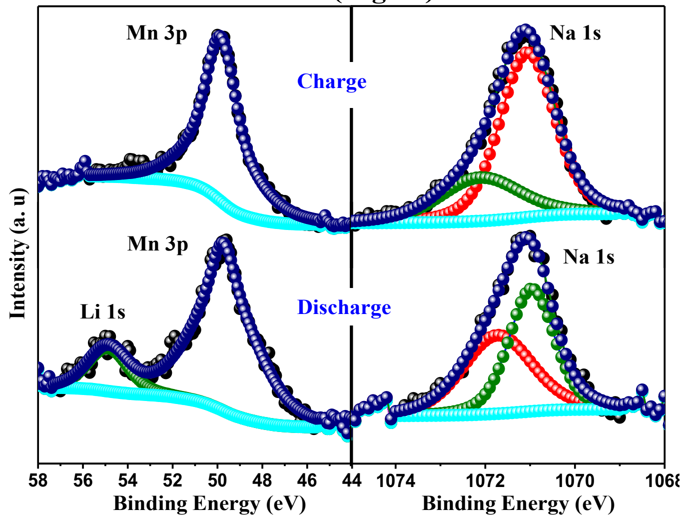
$Na_2Mn_3O_7$ | Li half cells offer 3.1 V operation with good cycling stability over 200 cycles

Li insertion into $Na_2Mn_3O_7$ layered oxide



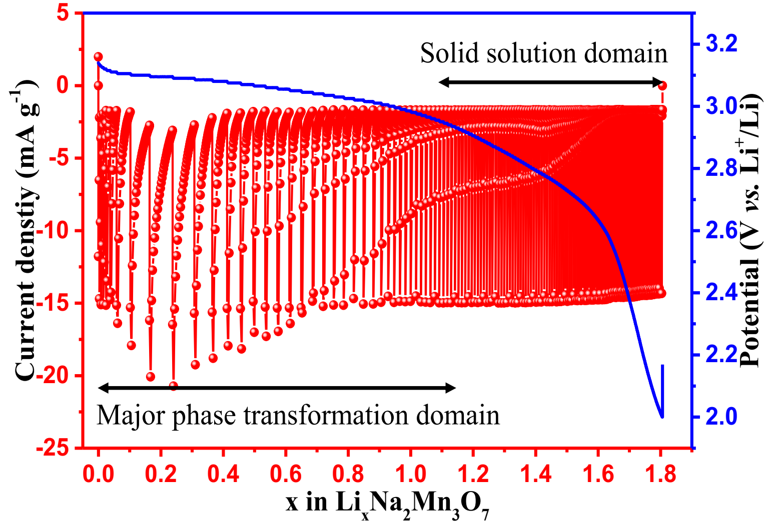


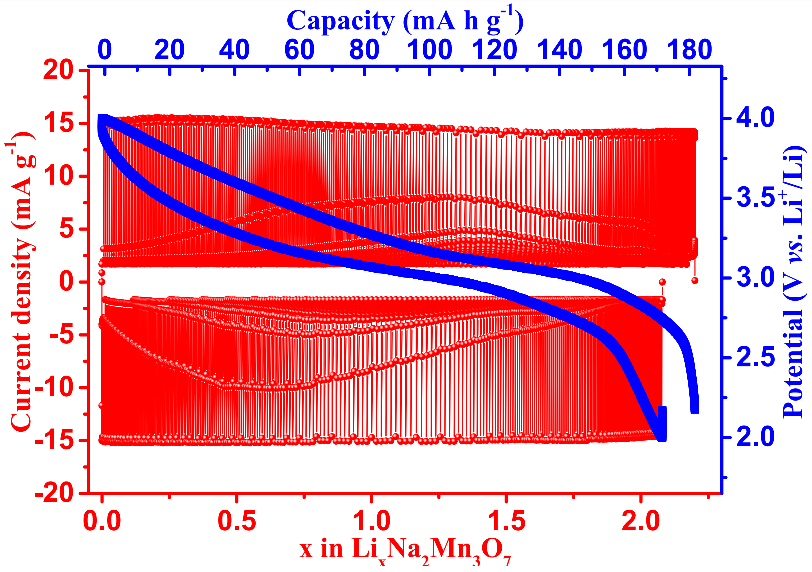


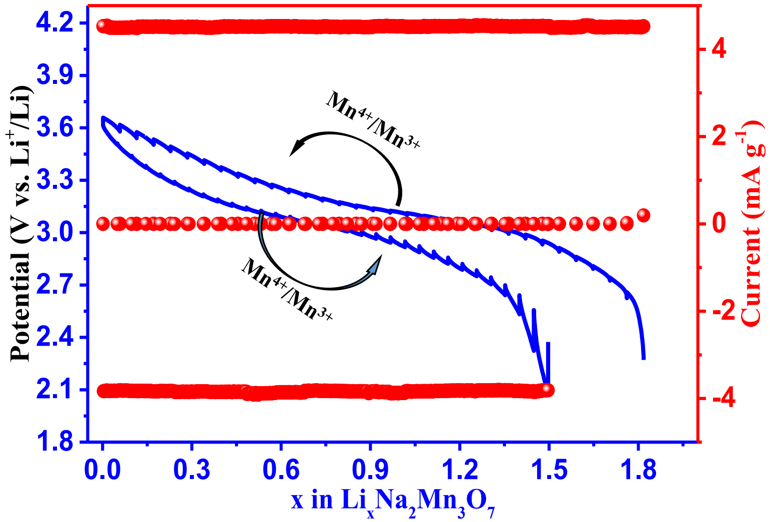


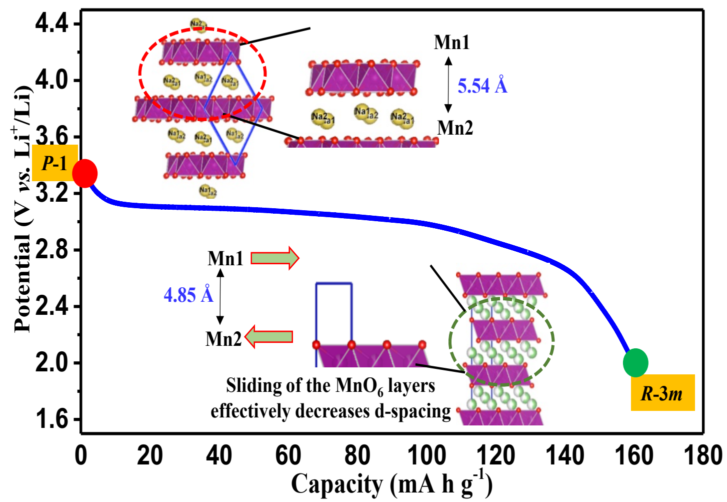
$Na_2Mn_3O_7$ | Li half cells : * undergo triclinic to trigonal structure offer 3.1 V operation
* XPS analysis confirms (de)lithiation with steady Na content

Li insertion into $Na_2Mn_3O_7$ layered oxide







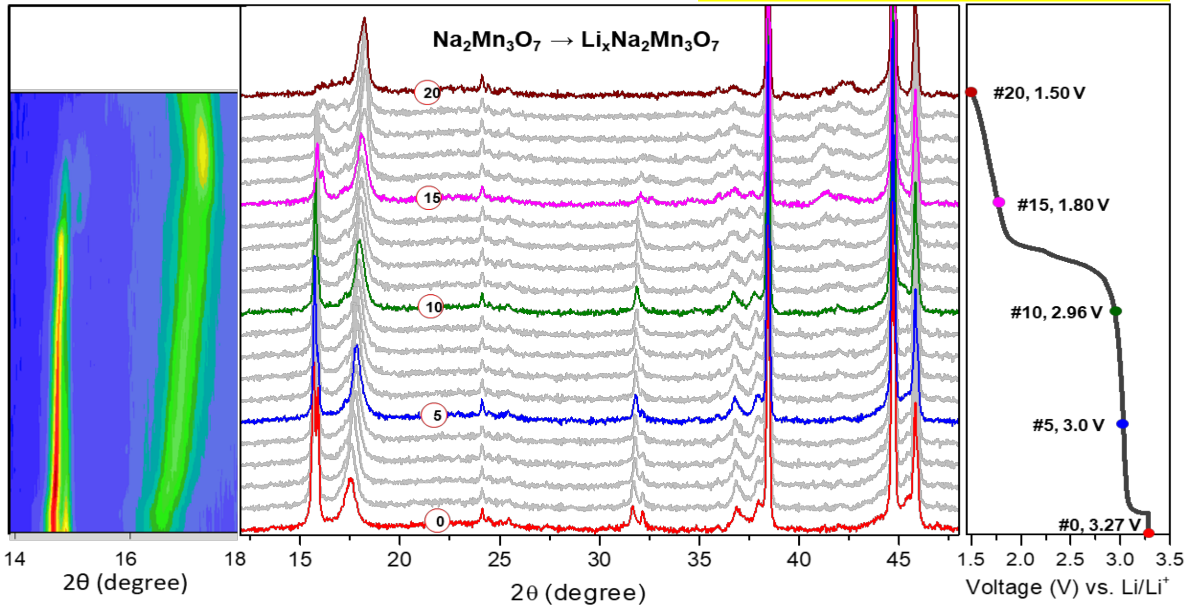


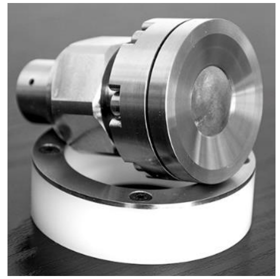
$Na_2Mn_3O_7$ | Li half cells :
* undergo triclinic to trigonal structure offer 3.1 V operation
* Involves solid-solution (single-phase) redox mechanism

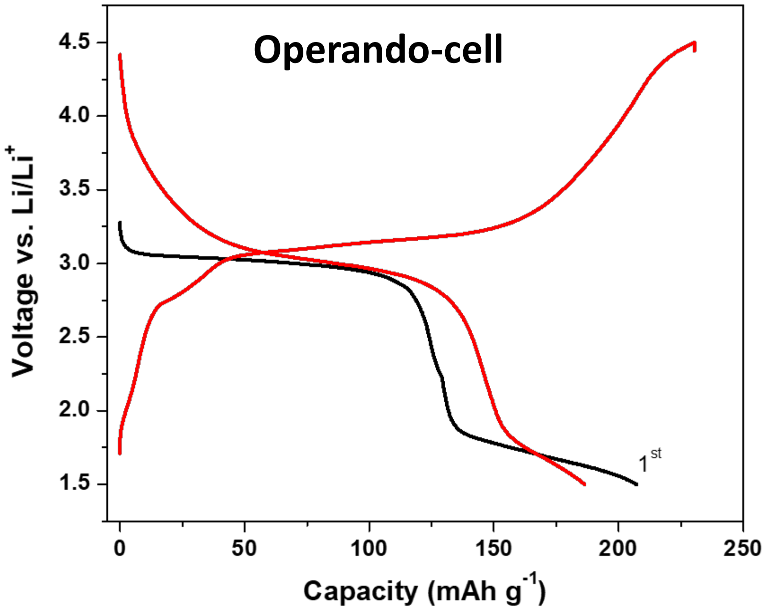
$Na_2Mn_3O_7$ work as a 3.1 V lithium-insertion host material

Li insertion into $Na_2Mn_3O_7$ layered oxide

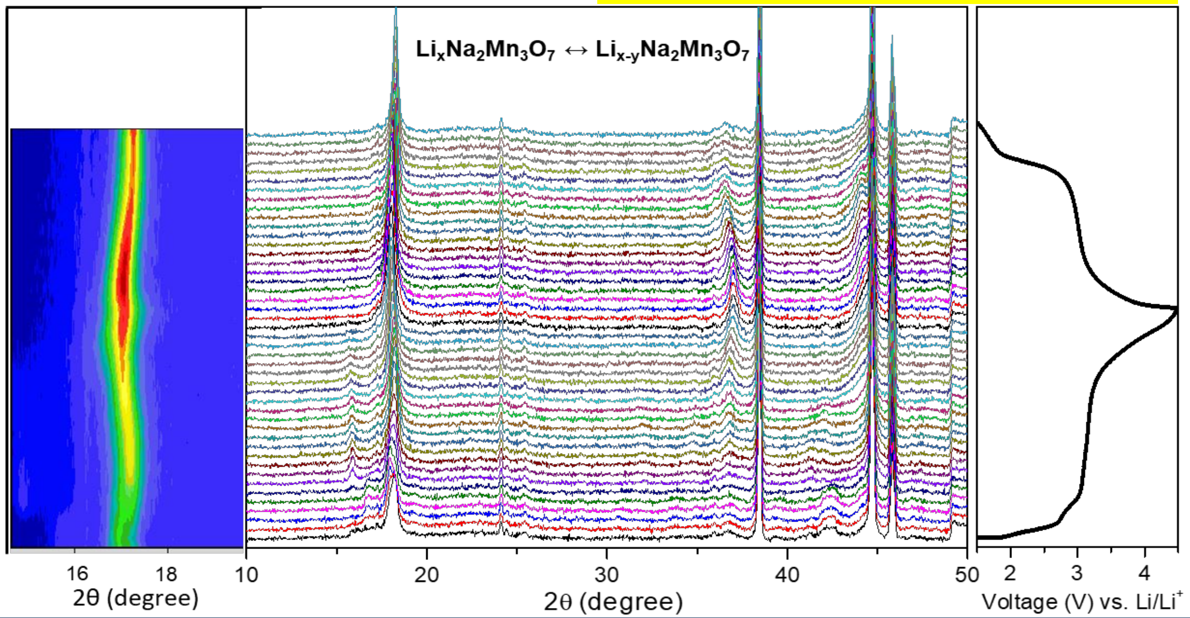
1st Discharge: Bi-phasic





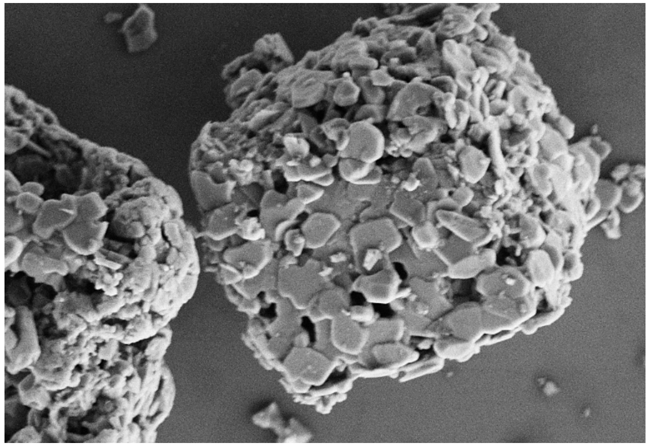


2nd (Dis)charge: monophasic

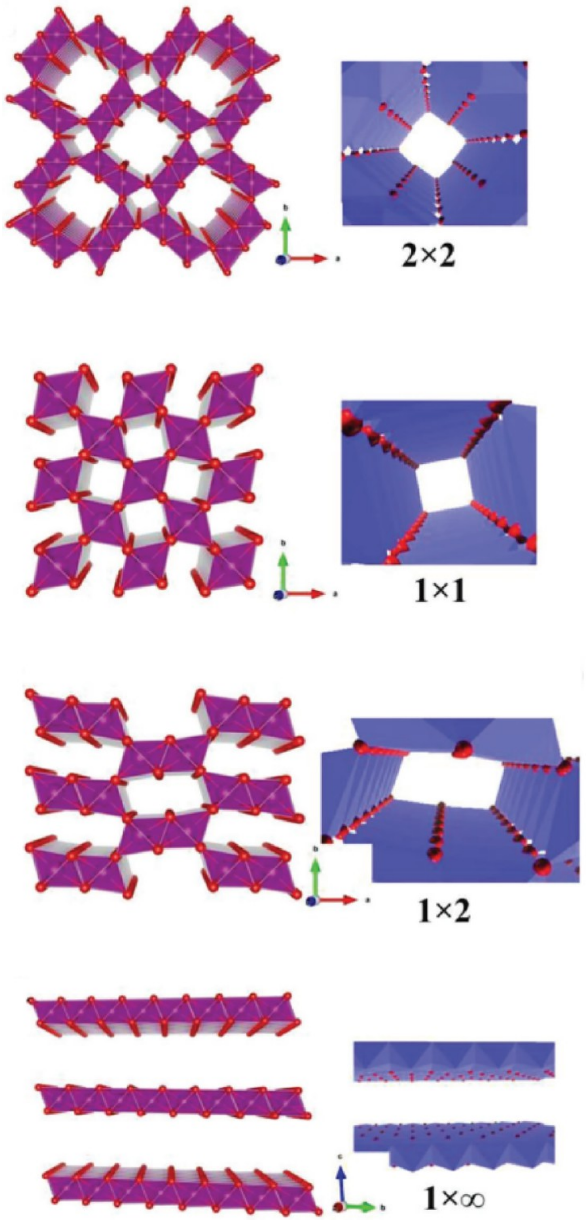


$Na_2Mn_3O_7$ | Li half cells:
Two redox ~ 200 mAh/g
Mn(II) – Mn(III) – **Mn(IV)**

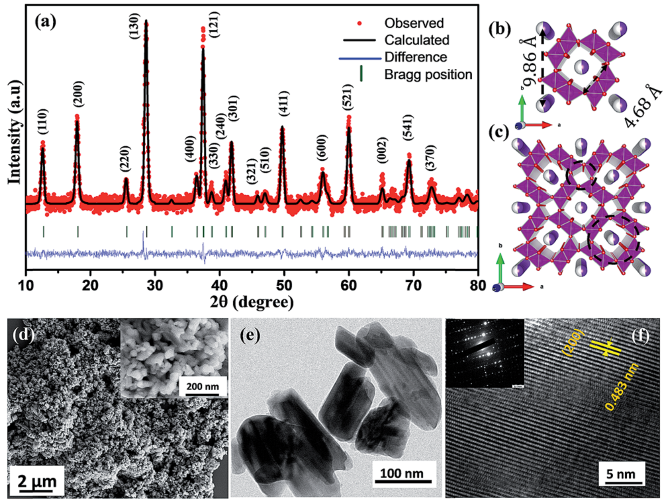
V. $Na_2Mn_3O_7$: An 1.4 V Zinc Insertion Material

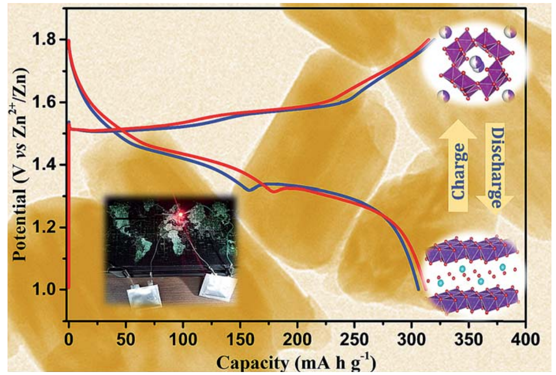


* K. Sada, B. Senthilkumar, P. Barpanda, Manuscript Submitted.

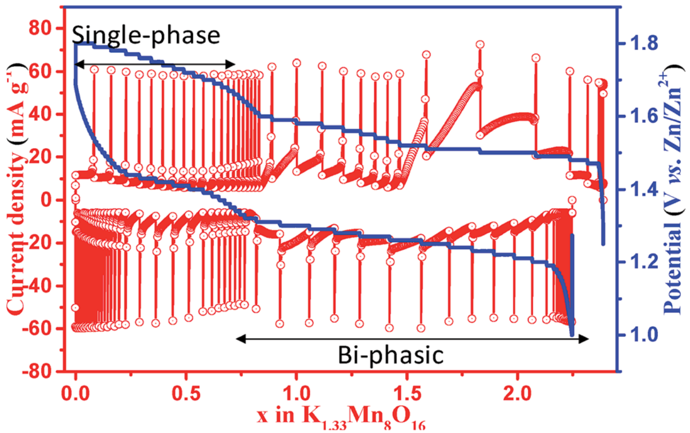


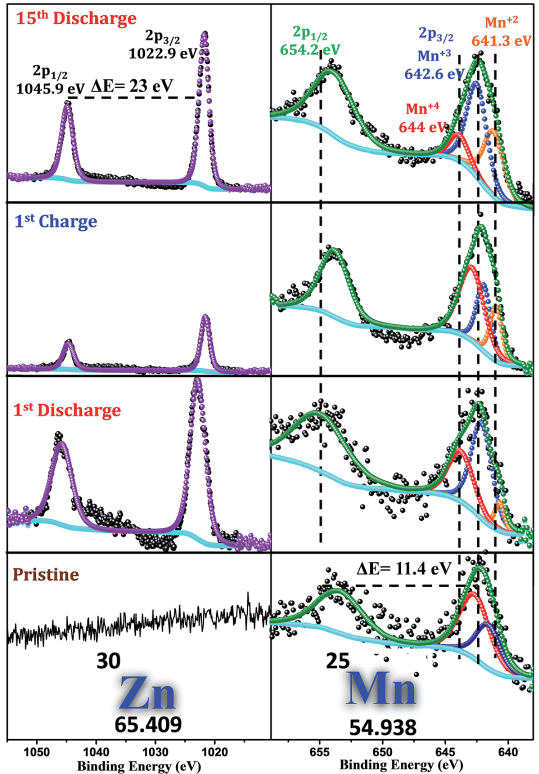
Cryptomelane $K_{1.33}Mn_8O_{16}$ (K_zMnO_2)





* Cryptomelane --- Birnessite
(tunnel) (layer)
* 1.5 V (vs. Zn) 2M $ZnSO_4$+1M $MnSO_4$





* K. Sada, B. Senthilkumar, P. Barpanda, *J. Mater. Chem. A.*, In Press, 2019.
(2019 Early Career Investigators Special Issue)

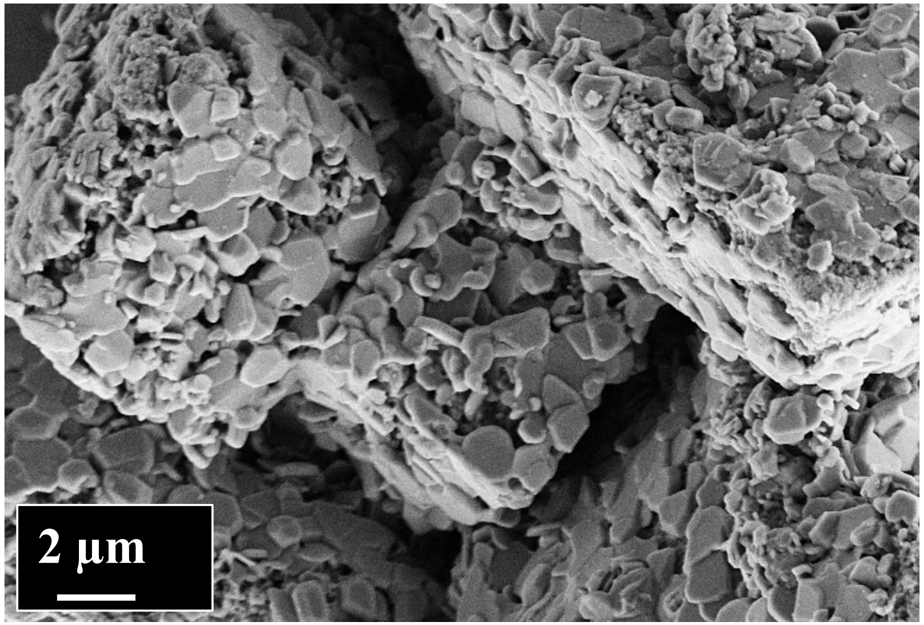
Hydrothermal Synthesis of $Na_2Mn_3O_7$ Cubes for ZIBs

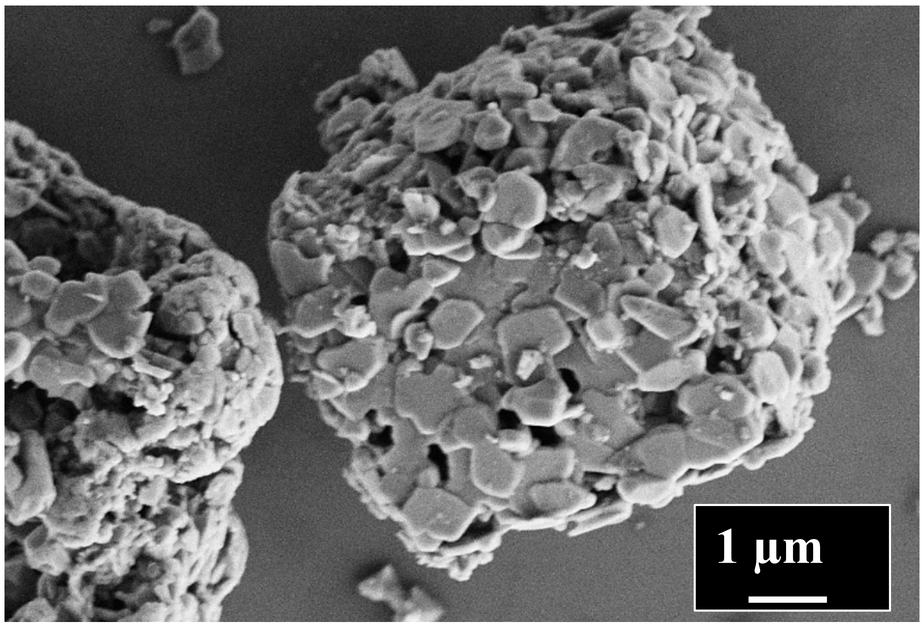
Step-1

- ✓ 0.2M $MnCl_2$ + 0.1M Urea (NH_2CONH_2) in distilled H_2O
- ✓ Calcined for 5 h at 180 ˚C
- ✓ Resulted $MnCO_3$ cubes

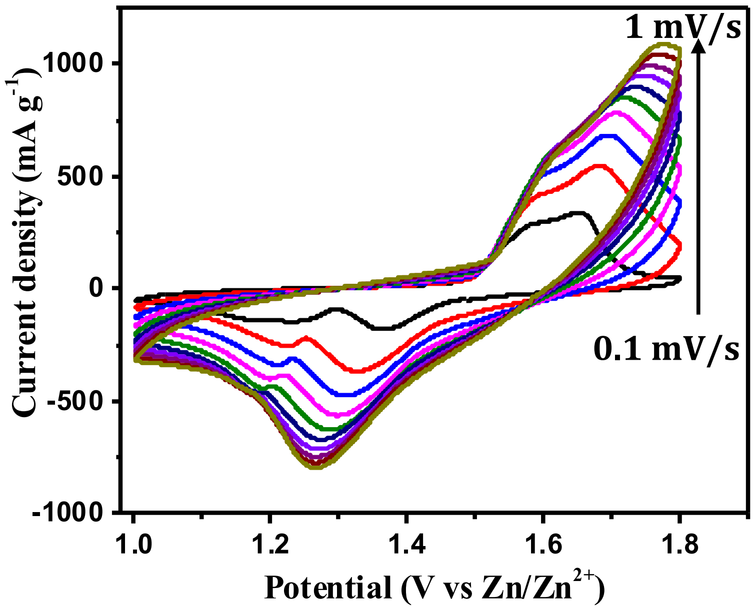
Step-2

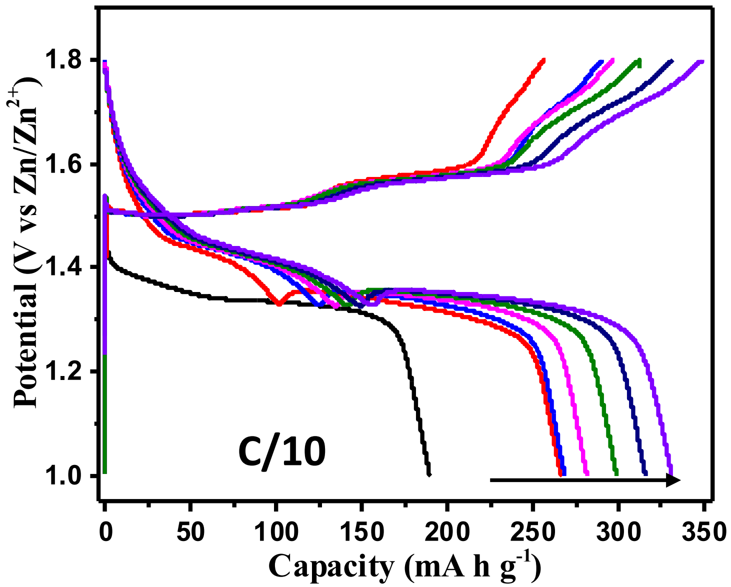
- ✓ $3\ MnCO_3 + 2\ NaNO_3 \xrightarrow[4\ h]{600\ ^\circ C} Na_2Mn_3O_7$

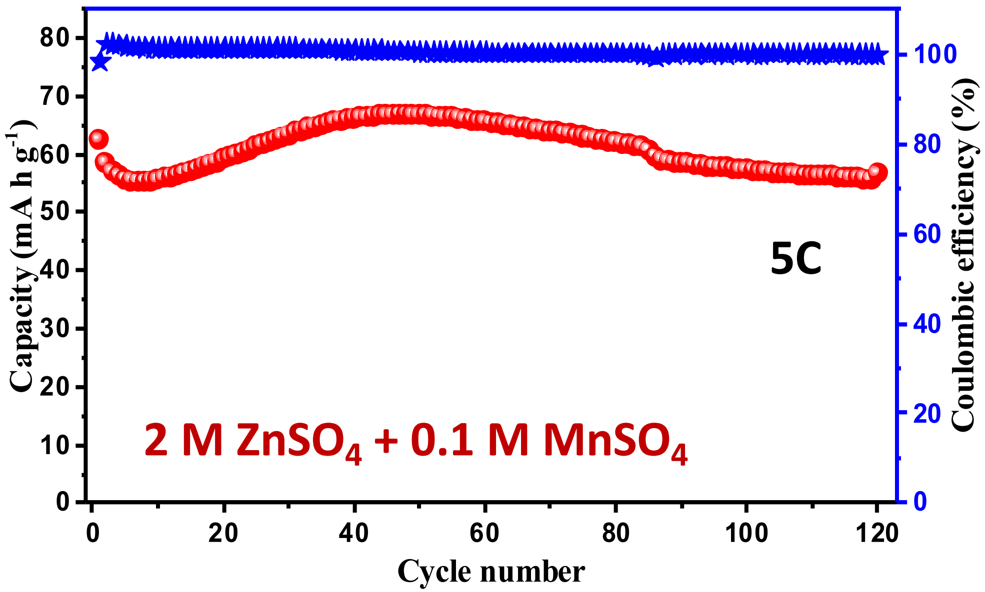




Zn insertion into $Na_2Mn_3O_7$ layered oxide

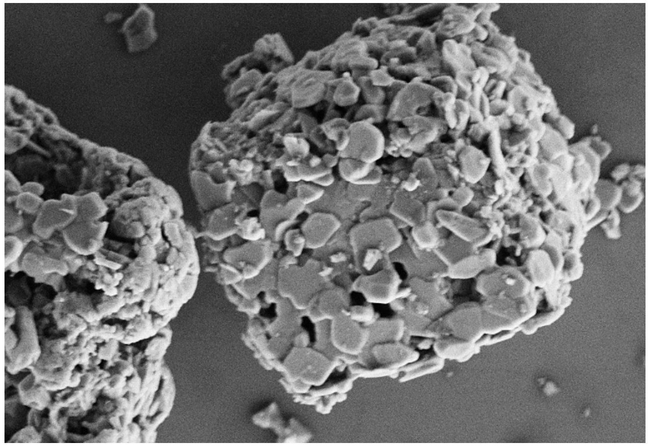






$Na_2Mn_3O_7$ work as a ~1.4 V zinc-insertion host material

VI. $Na_2Mn_3O_7$: An Aqueous Li Insertion Material

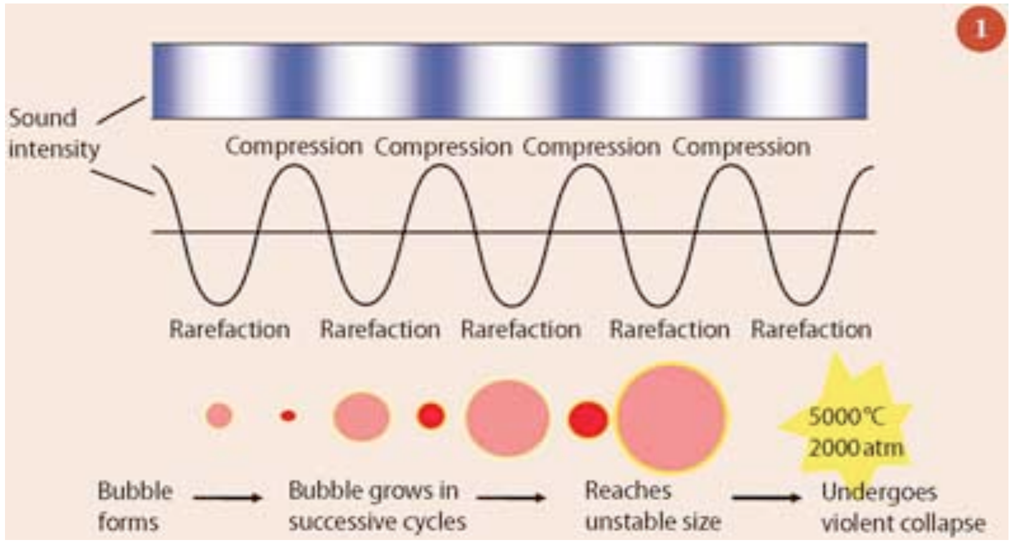


* K. Sada, B. Senthilkumar, P. Barpanda, Manuscript Submitted.

(Ultrasonic) Sonochemical Synthesis

Ultrasonic Sonochemical Synthesis (USS)

(SONICS^{TM} Sonicator)



Precursor Sol/Suspension → Sonication → **Sonicated Product** → Annealing → **Final Product**

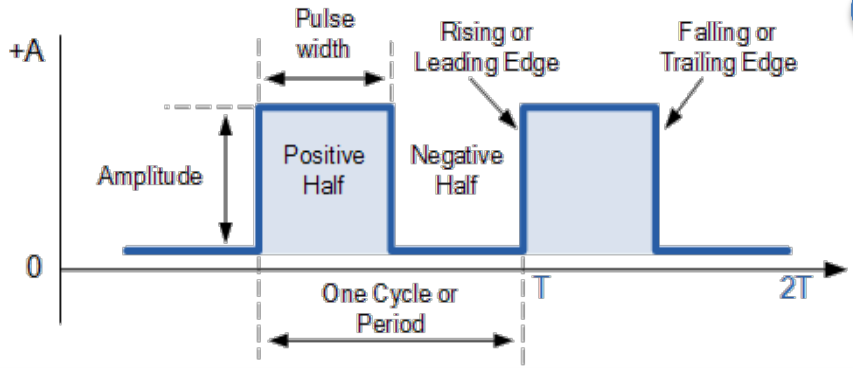
Reacting Media

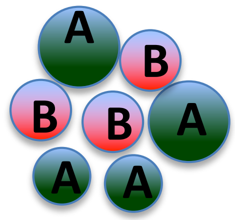
Precursor Solubility

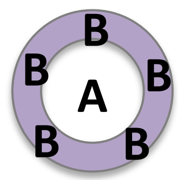
Soluble — **Partly Soluble** — **Insoluble**

e.g. **- Water**
- Isopropylalcohol
- Acetone

Sonic Wave

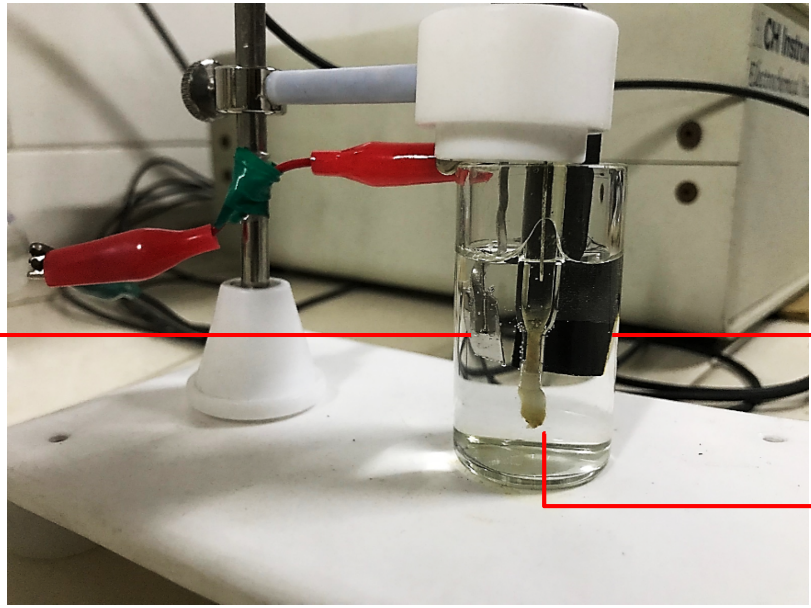




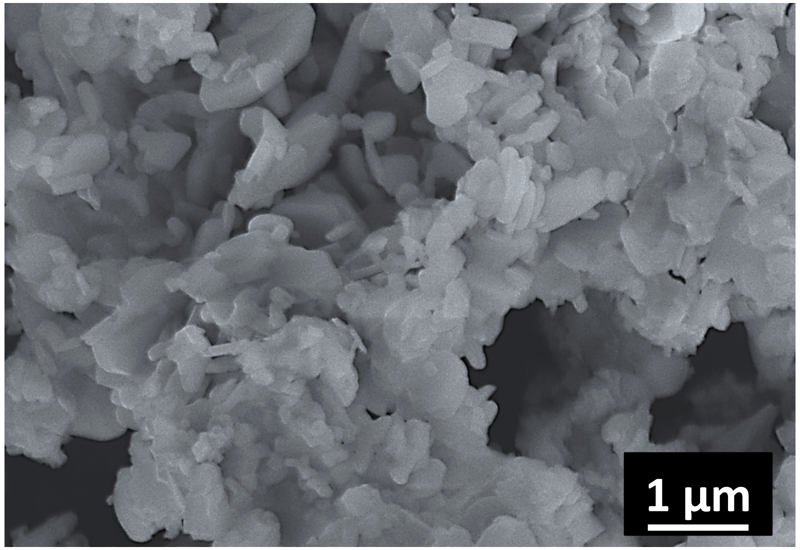


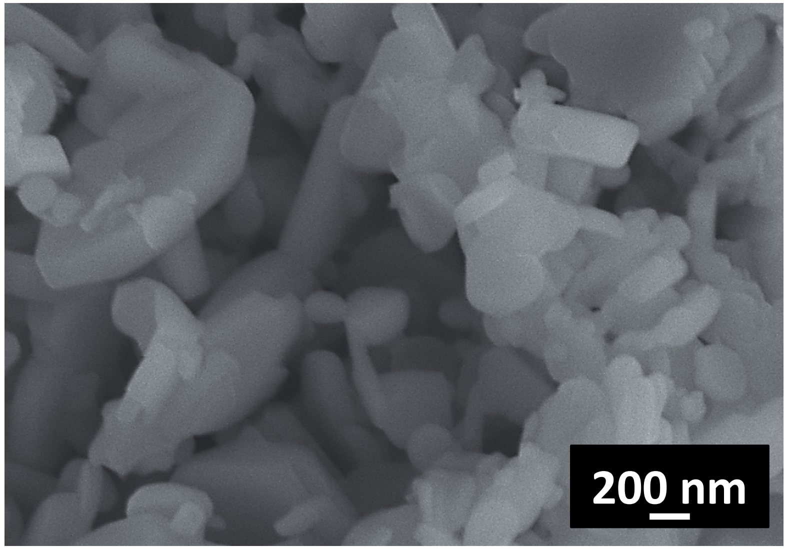
Sonochemical Synthesis: zeolites, oxides, inorganic compounds, ferrites etc.

Sonochemical Synthesis of $Na_2Mn_3O_7$ for aqueous batteries

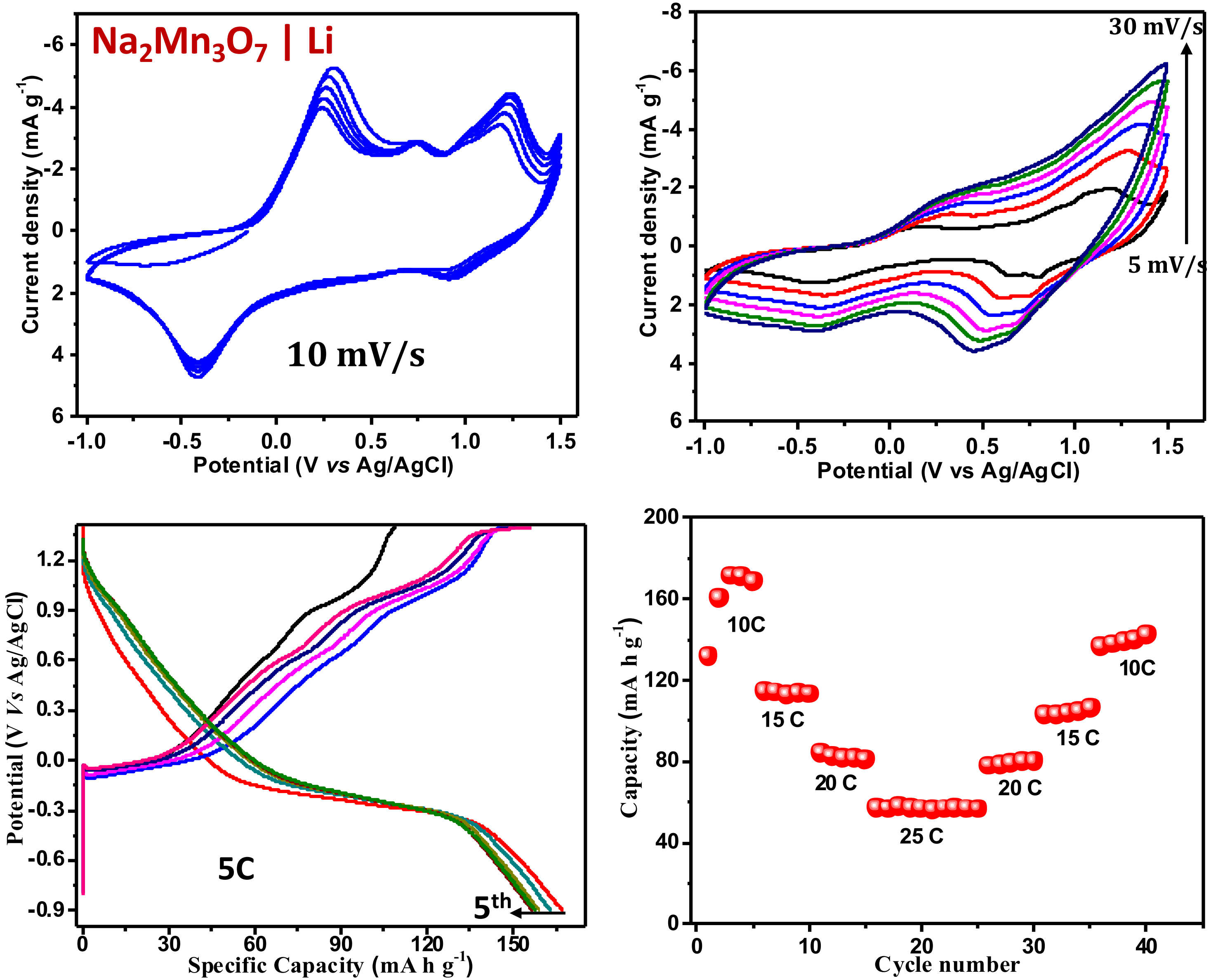


Aqueous electrolyte: 1M Li_2SO_4
1M Na_2SO_4
1M K_2SO_4





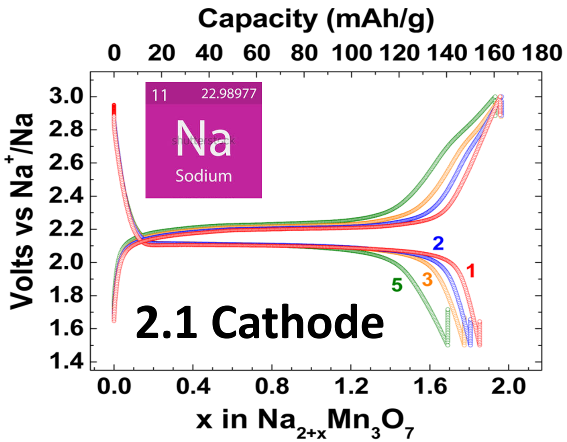
Designing aqueous batteries with $Na_2Mn_3O_7$ layered oxide



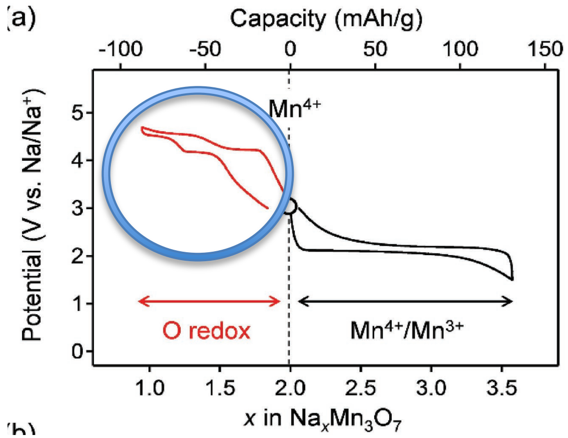
$Na_2Mn_3O_7$ work as an efficient insertion host in aqueous batteries

Versatile $Na_2Mn_3O_7$ Insertion Material

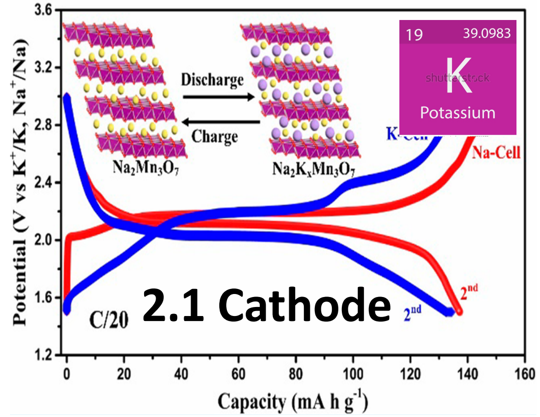
I. Sodium-ion Batteries



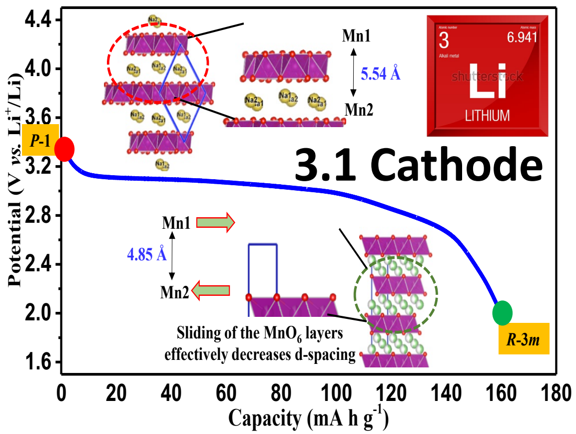
II. Anionic Redox Activity



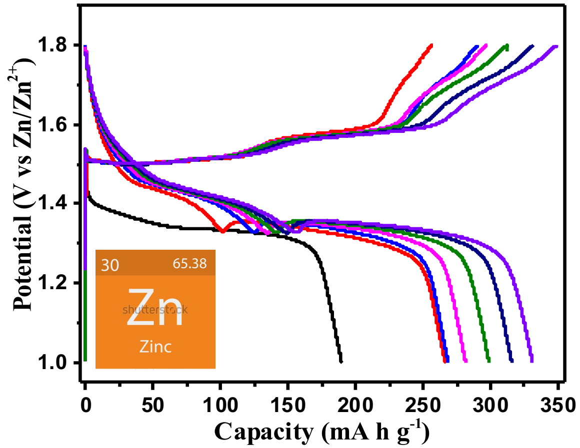
III. Potassium-ion Batteries



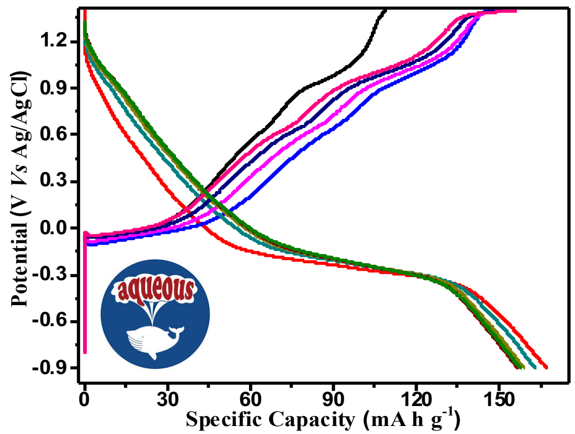
Layered Triclinic (*P*-1) $Na_2Mn_3O_7$



IV. Lithium-ion Batteries



V. Zinc-ion Batteries



VI. Aqueous Batteries

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* Prof. Evgeny Antipov
* Prof. Artem Abakumov
* Prof. Keith Stevenson

Spaciba **| Thank You for Your Kind Attention**