Battery Safety Science Webinar Series

Advancing safer energy storage through science

Feb. 17, 2021: 5.00 p.m. (EST) | Feb. 18, 2021: 6 a.m. (Singapore Time)

Sodium-ion Battery: From Materials to Cell Development

Host **Kanarindhana Kathirvel (Rindhu)**
Sr. Project Management Specialist, Underwriters Laboratories

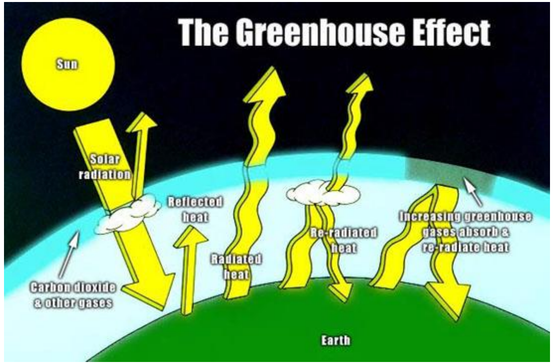
Presenter **Dr. Palani Balaya**
Associate Professor, Department of Mechanical Engineering,
Faculty of Engineering, National University of Singapore

UNDERWRITERS LABORATORIES™

Contents

- Need for energy storage systems
- Li-ion Battery: What limits 100% DoD?
- Na-ion Battery:
  - Na_2MnSiO_4
  - Voltage Step Phenomenon
  - Non-flammable electrolyte
  - Doped $Na_3V_2(PO_4)_3$ cathode
  - O3 – type cathode
- Take home message

Climate Change Issues

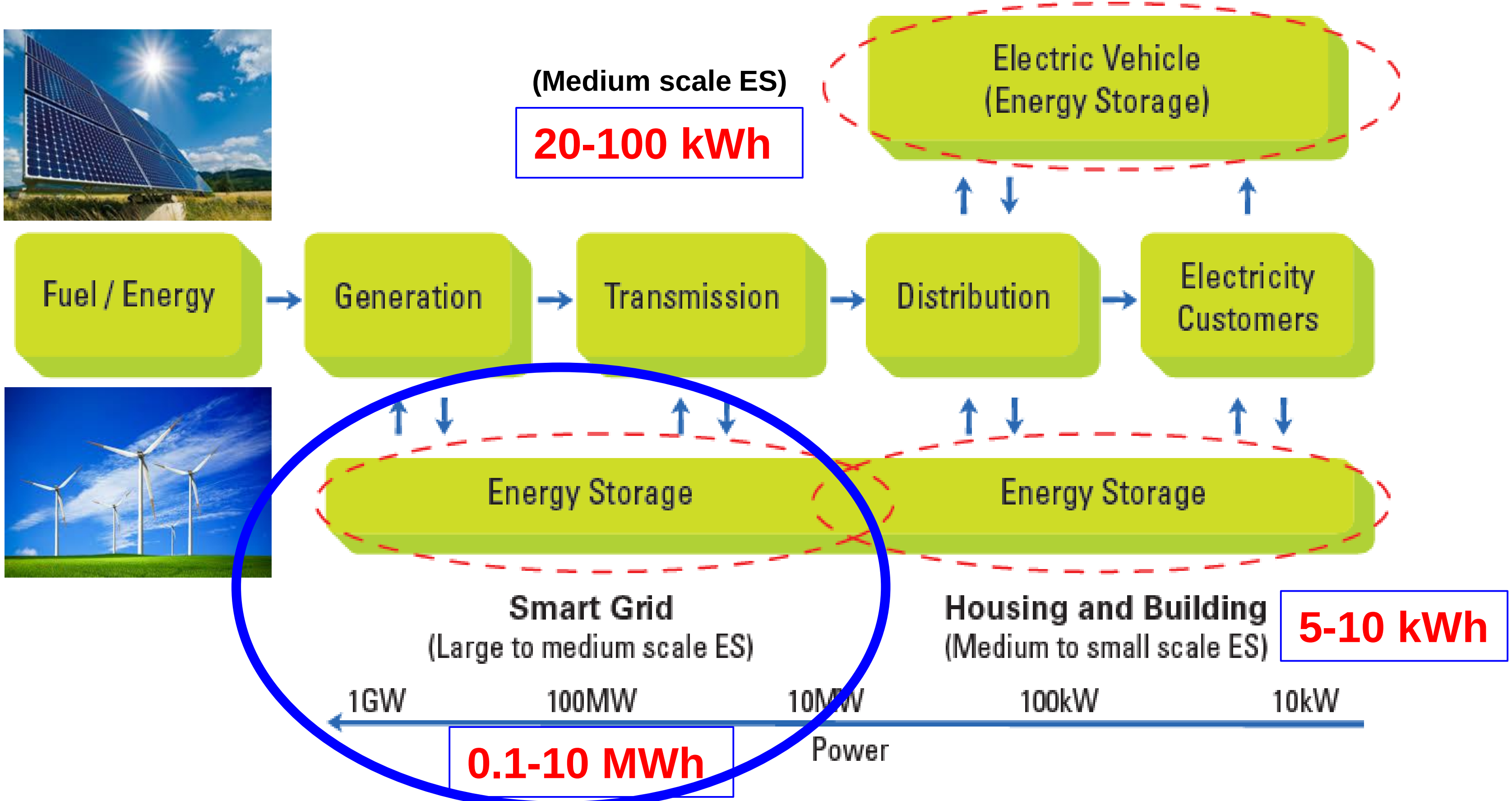


Need to reduce CO_2 emission

Renewable Energy Options[1]

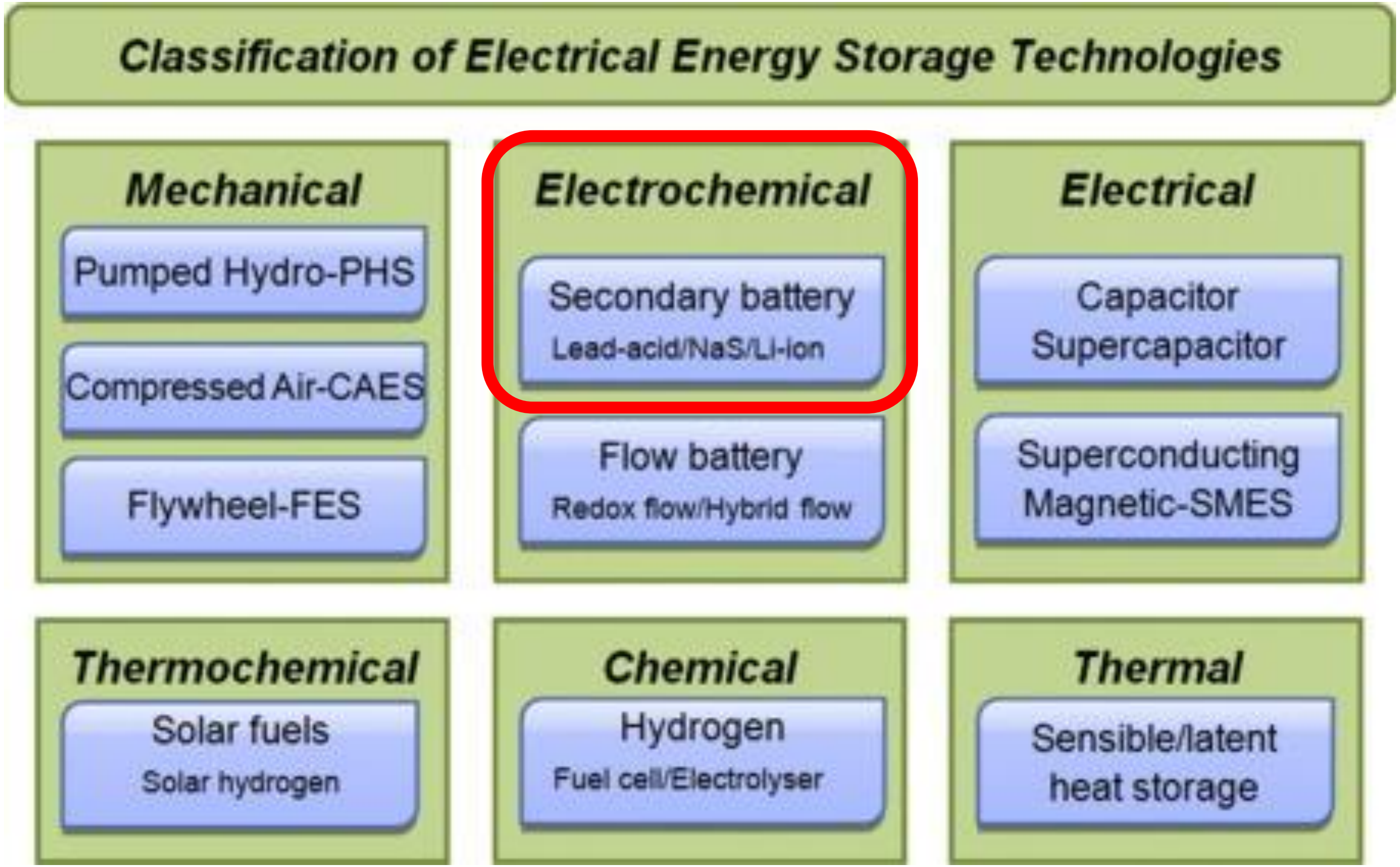
[1]IPCC-Special Report on Renewable Energy for Climate Change Mitigation (2011)

Renewable Energy: Electricity Value Chain[2]



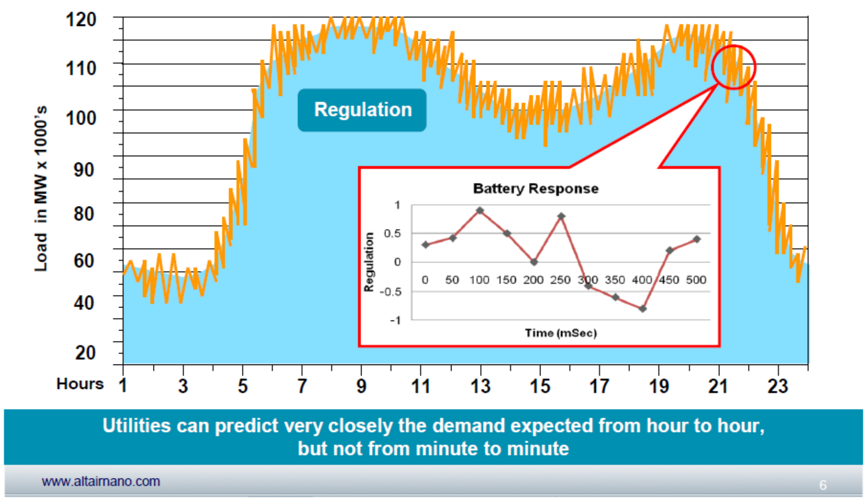
[2]Energy Storage Tech Primer, Singapore 2011

Storage Type Grouped by Technology



Large scale storage systems (solar and wind power)

INTERMITTENCY



Energy storage systems

Frequency Regulation:

To smoothen and improve the quality of the grid power

Target for Micro-grids:
- 0.1 – 1 MWh
- 4C-5C (15-12 min.)
- 5000 (@ 1C) cycle life
- Safety
- Inexpensive

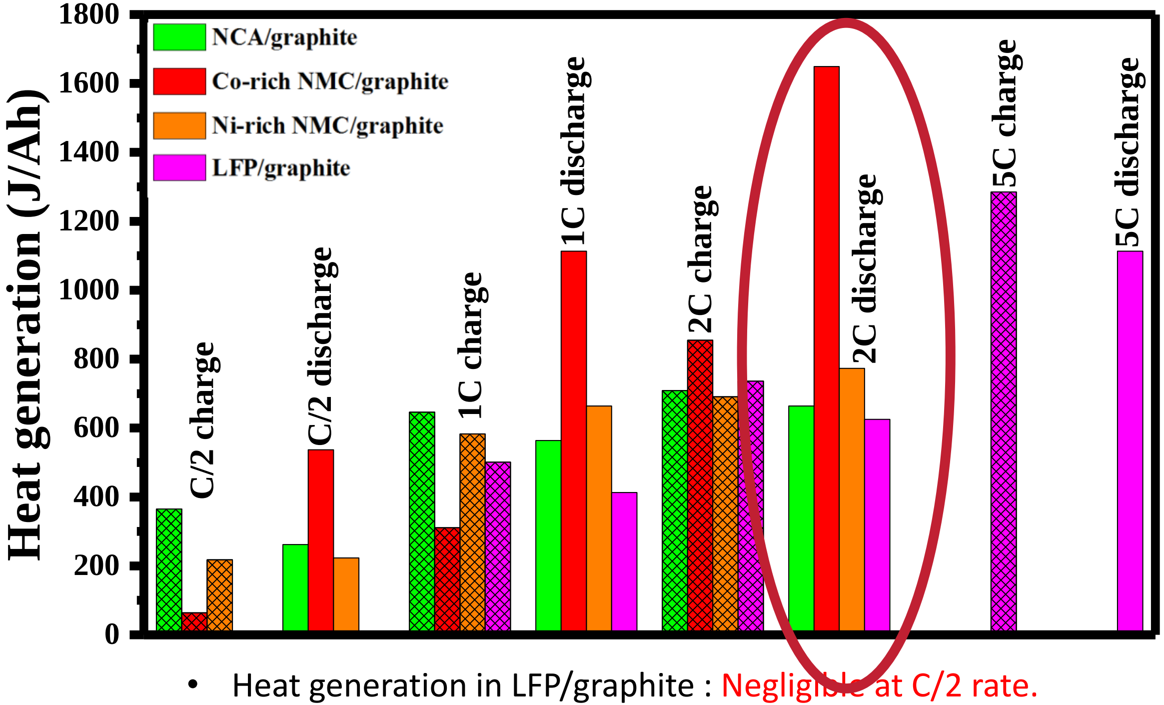
http://www.powermag.com/battery-storage-goes-mainstream-2/

Li-ion Battery Chemistries:

- **NCA/graphite**
- **Co-rich NMC/graphite**
- **Ni-rich NMC/graphite**
- **$LiFePO_4$/graphite**

What limits 100% DoD?

Total Heat Generation:
Different Li-ion Cell Chemistries at Various C-rates

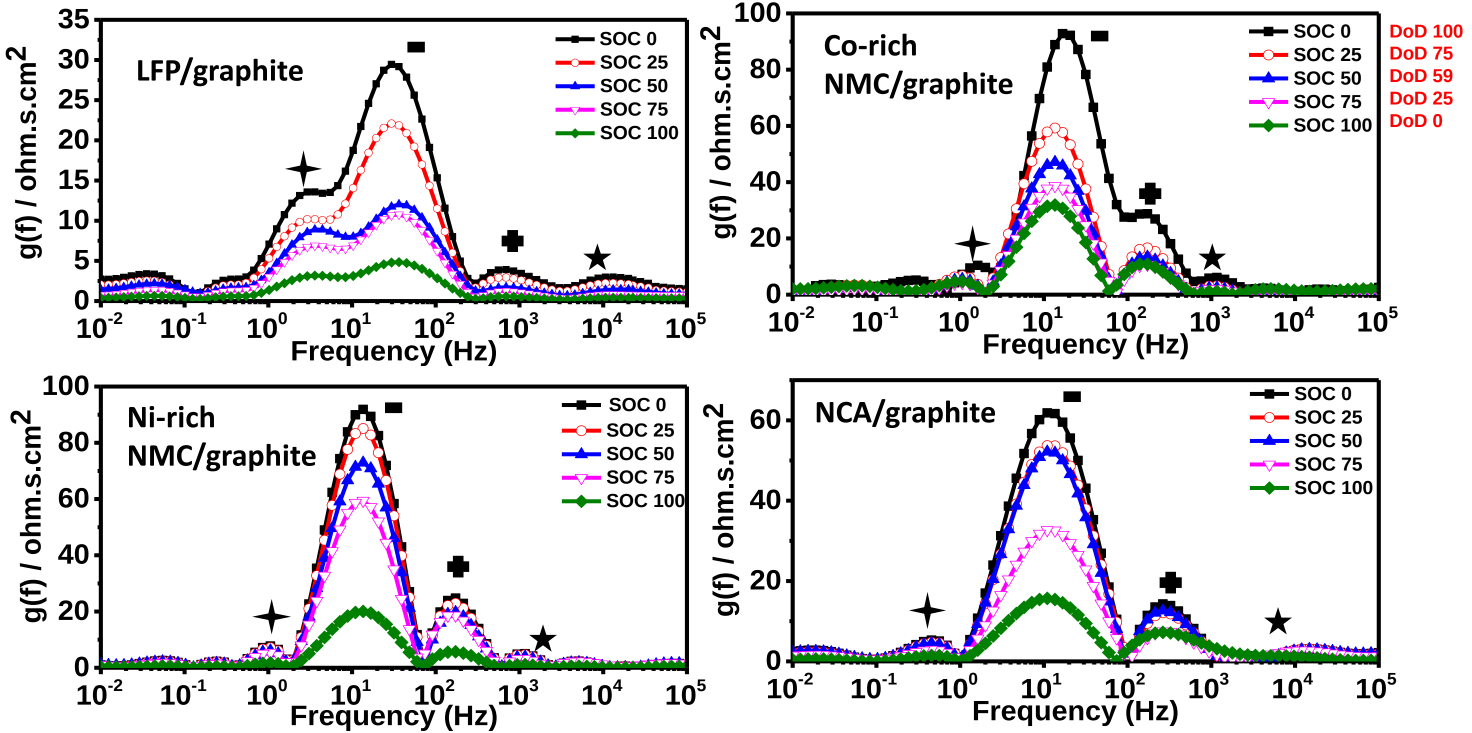


- Heat generation in LFP/graphite : Negligible at C/2 rate.
- Cyclability until 5C rate is only possible in LFP/graphite.
- In Co-rich NMC/graphite Q_{disch} >>> Q_{ch}

Co rich NMC /graphite > Ni rich NMC/graphite > NCA/graphite > LFP/graphite

B. Manikandan, C. Yap, P. Balaya, *J. Electrochem. Soc.*, **164** (2017) A2794.

18650 Li-ion Cells of Different Chemistries:
Impedance data analysis using Distributed Relaxation Time method



Below 10 Hz - Solid state diffusion resistance ✦

10^1-10^2 Hz - Charge transfer polarization ▬

10^2-10^3 Hz – Passivation layer resistance ✚

Above 10^3 Hz – Contact resistance ★

B. Manikandan, V. Ramar, C. Yap, P. Balaya, *J. Power Sources*, **361** (2017) 300.

g(f) – distribution function

SODIUM-ION BATTERY

How can sodium-ion battery help?

Material resources	Reserves (kilotons)	Years left	Cost of respective battery $US/kWh
Lithium compound	4100	~150	~500-700 (LTO)
Sodium compound	3,300,000	>1000	200-300

For High power applications

- # Na_2MnSiO_4

Journal of Power Sources 359 (2017) 277–284

ELSEVIER

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Na_2MnSiO_4 as an attractive high capacity cathode material for sodium-ion battery

CrossMark

Markas Law, Vishwanathan Ramar, Palani Balaya*

Department of Mechanical Engineering, National University of Singapore, 117575, Singapore

Na_2MnSiO_4: Synthesis & characterization

In-house Mn_2SiO_4

↓

Na_2CO_3 + Glucose

↓

Ball mill
500 rpm, 30 mins

↓

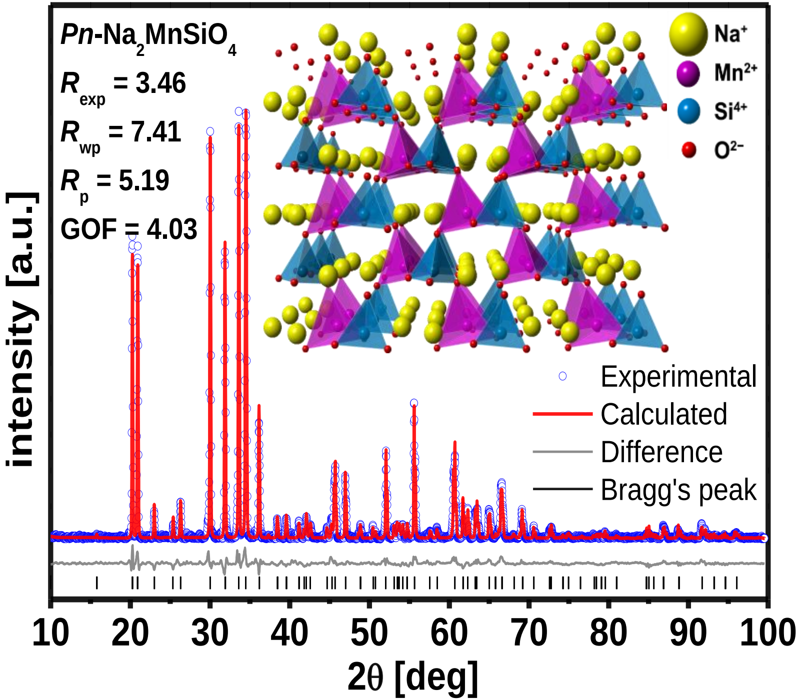
Calcination: 750°C for 8h; in argon

↓

Carbon black Super P

↓

Ball mill
500 rpm, 4 h

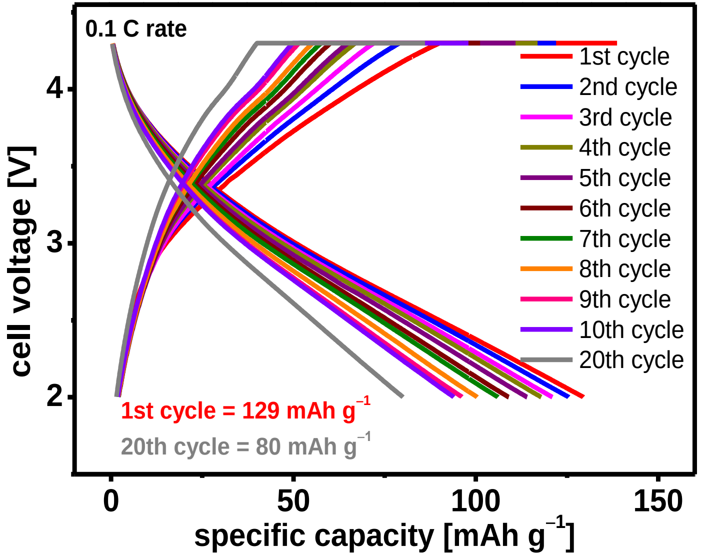


Rietveld refinement:

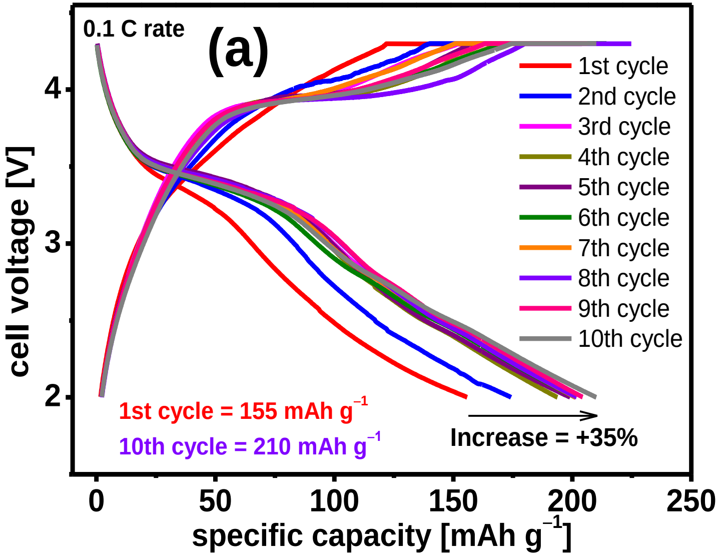
Na_2MnSiO_4 has a monoclinic crystal structure with space group *Pn*.

Sodium storage performance

Electrolyte: $NaPF_6$ in EC:PC, with no VC



Electrolyte: $NaPF_6$ in EC:PC, with 5 vol% VC



$NaPF_6$ in EC:PC, no VC

It is clearly seen no increase in discharge capacity is observed, even after 20 cycles.

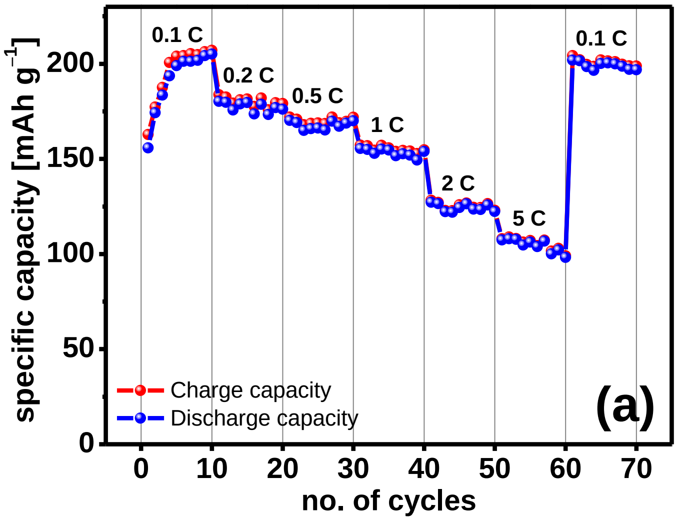
$NaPF_6$ in EC:PC + 5 vol%

As cycling progresses, a charge plateau begins to appear at ~3.9 V resulting in an increase in charge capacity.

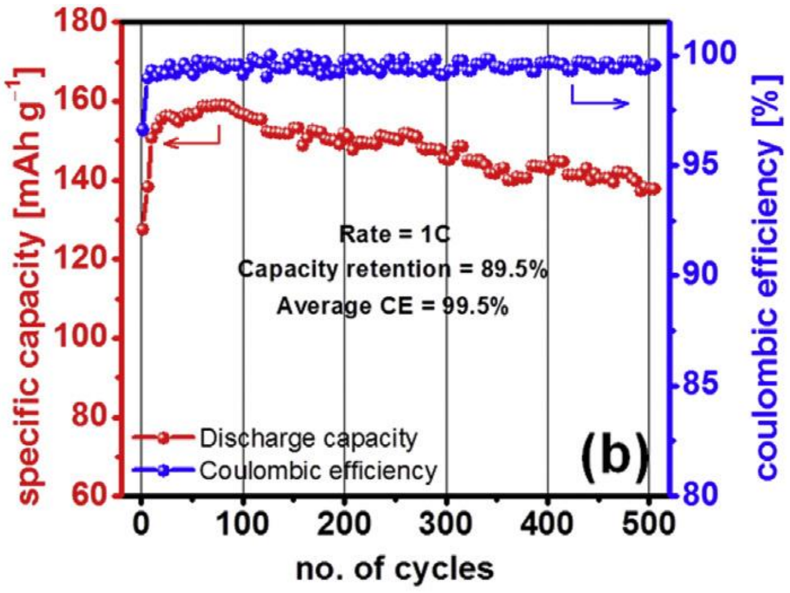
Discharge capacity increases to 210 mAh g^{-1} in the 10th cycle, involving 1.5 moles of Na^+.

J.C. Burns…J. R. Dahn, *J Electrochem. Soc.* **160** (2013) A1668.

Sodium storage performance



- NMS sample demonstrates high and stable discharge capacities at various current rates
- At a high 5 C rate, the electrode is able to deliver close to 100 mAh g^{-1}

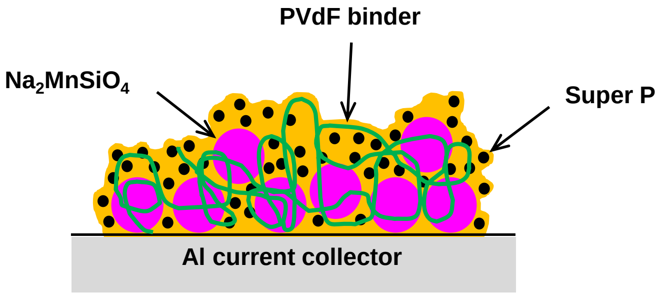


NMS electrode is able to withstand 500 cycles

Capacity retention close to 90% is achieved

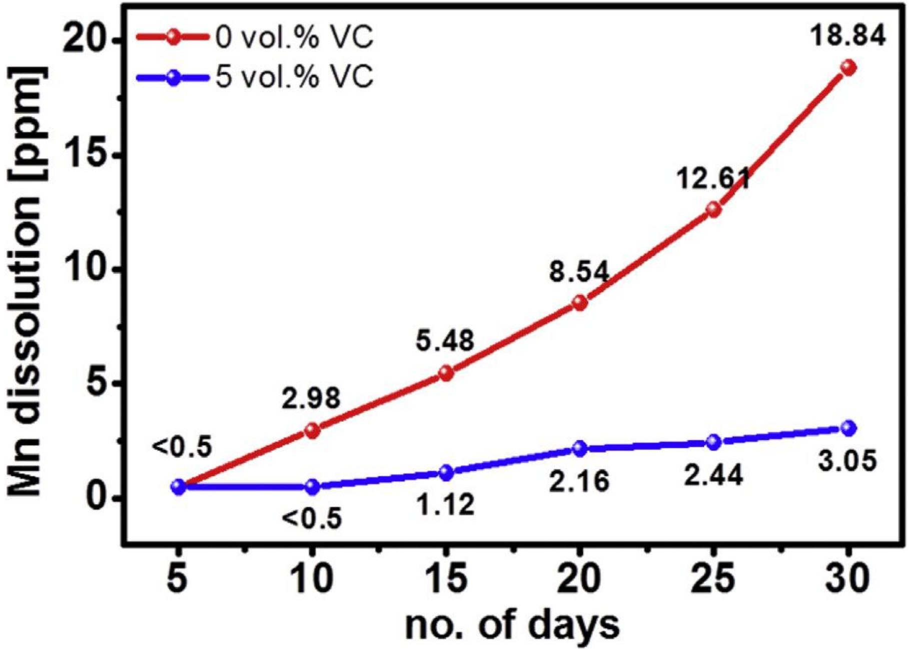
Average coulombic efficiency of 99.5% is achieved

Manganese dissolution



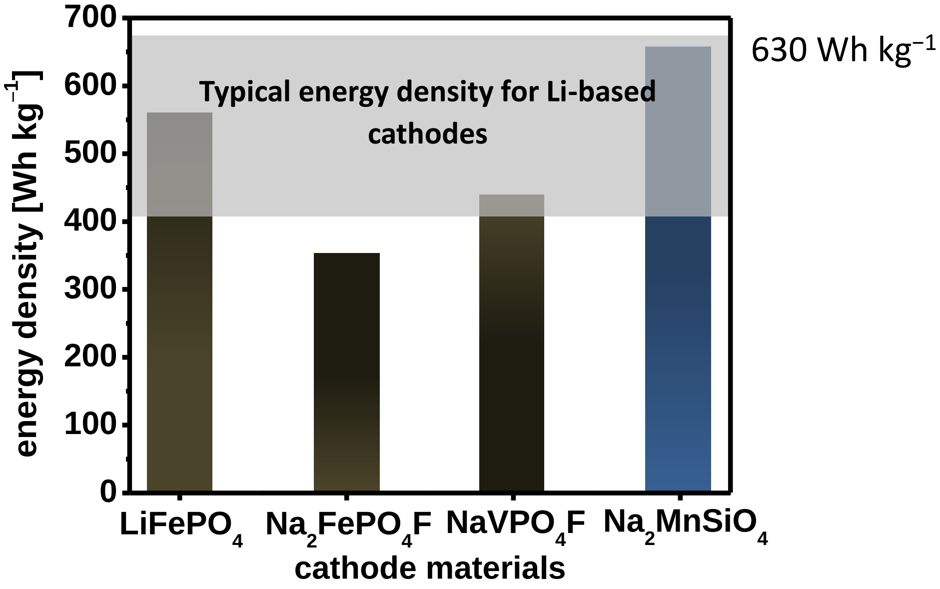
5 vol.% VC

When VC content is optimised, passivation film covers surface of electrode at just the right amount, leading to suppressed Mn dissolution.



J.C. Burns…J. R. Dahn, *J Electrochem. Soc.* **160** (2013) A1668.

Na_2MnSiO_4 – Summary



- Na_2MnSiO_4 – potential cathode material with energy density matching its lithium counterparts.

Na_2MnSiO_4	Discharge capacity = **210 mAh g $^{-1}$**
	~1.5 moles of Na^+
	Average redox potential = **3.0V**

• Voltage Step Phenomenon

Electrochemistry Communications 46 (2014) 56–59

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

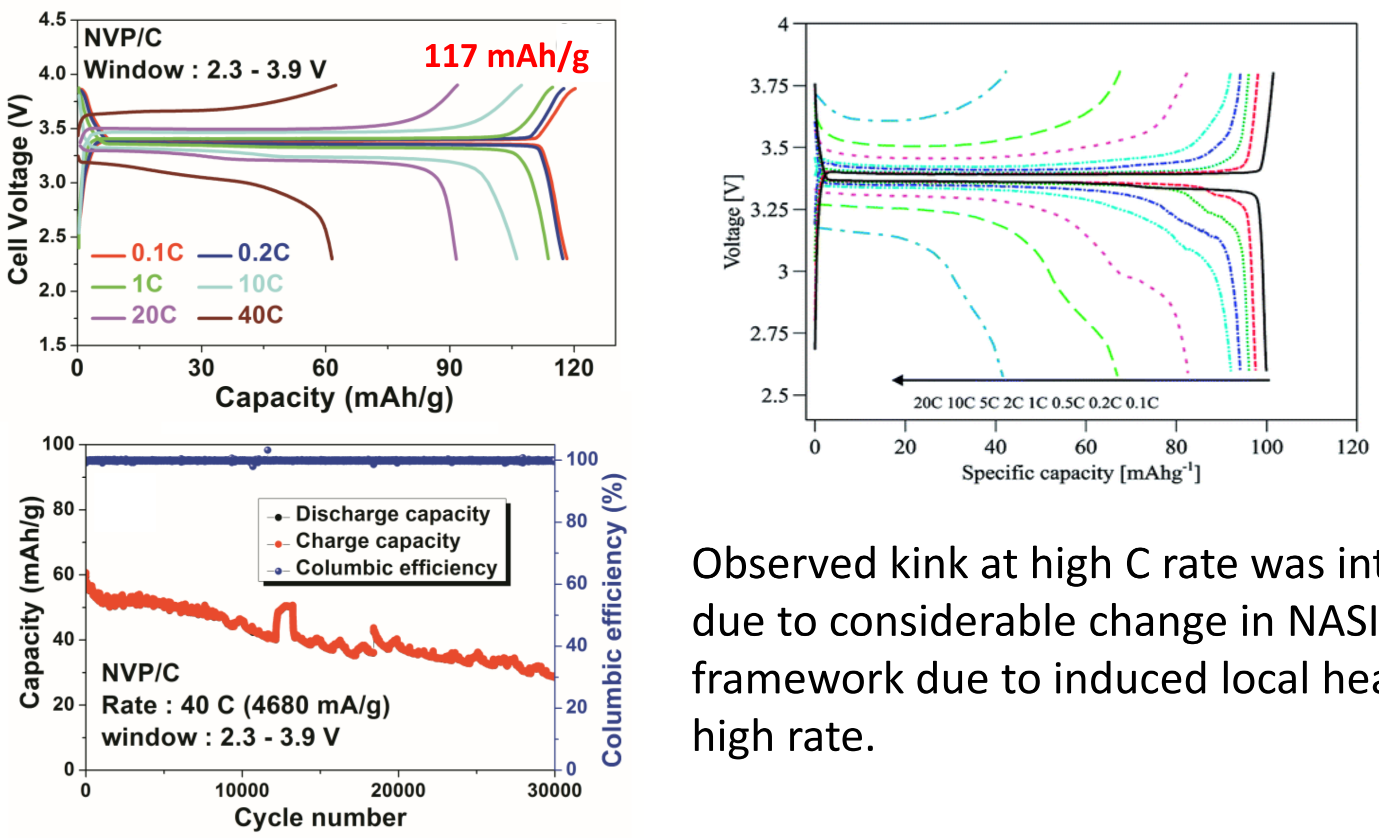
Short communication

A new phenomenon in sodium batteries: Voltage step due to solvent interaction

Ashish Rudola [a,1], Doron Aurbach [b], Palani Balaya [a,*]

[a] Department of Mechanical Engineering, National University of Singapore, Singapore 117576, Singapore
[b] Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel

Electrochemical characterization of $Na_3V_2(PO_4)_3$



Observed kink at high C rate was interpreted due to considerable change in NASICON framework due to induced local heating at high rate.

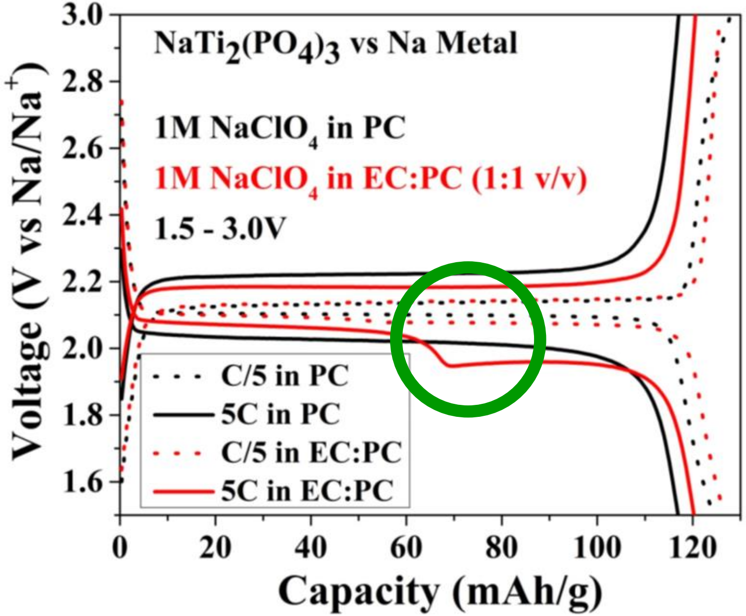
K. Saravanan,…P. Balaya, *Adv. Energy Mater*. **3** (2013) 444

X. Jiang,…J.Y. Lee, *J. Mater. Chem. A*, **4** (2016) 14669

Electrolyte influence on Na electrode

Voltage Step Phenomenon

using carbonate-based electrolyte solutions



Voltage step seen:

→ in EC:PC based solutions

→ at high C rates

→ only during discharge and not at charge cycle

→ not in PC based solution

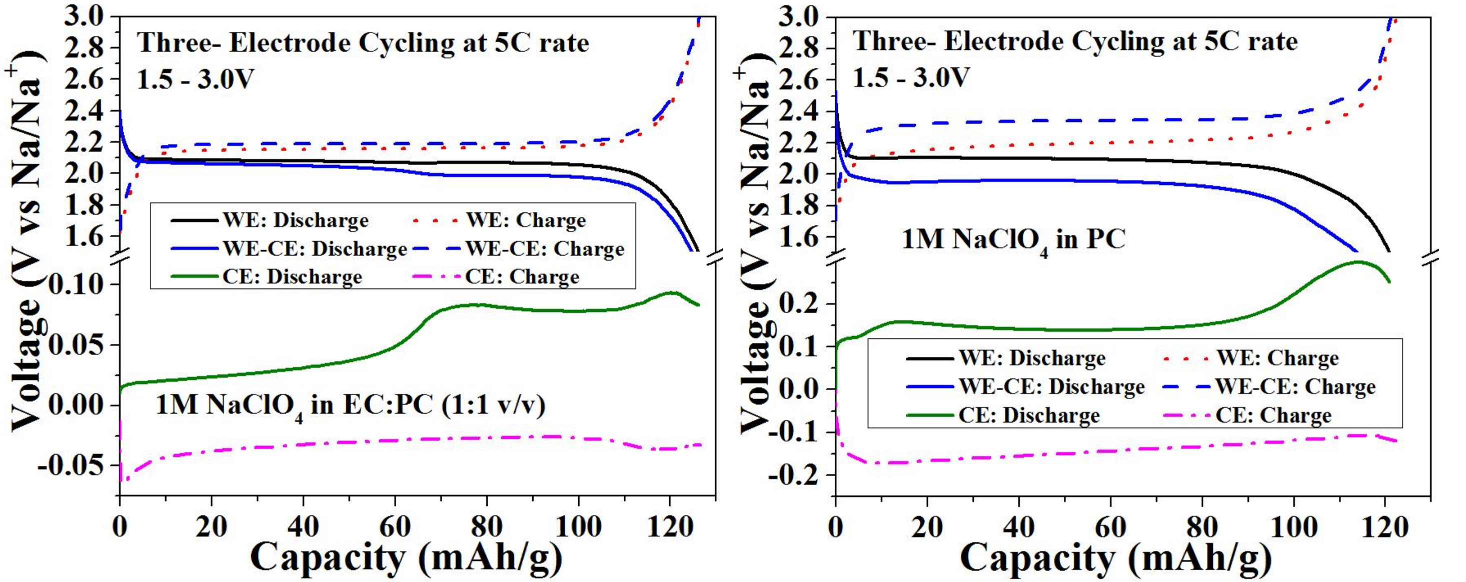
$NaTi_2(PO_4)_3$ working electrode (WE) interface appeared to be different in EC:PC and PC solutions?

Electrolyte influence on Na electrode

Surprisingly, the voltage step not caused by the NTP WE

→ caused by an increased polarization of the Na CE

WE = Working Electrode, CE = Counter Electrode, RE = Reference Electrode



Na CE covered with passivation layers in carbonate-based electrolyte solutions

A. Rudola, D. Aurbach and P. Balaya, *Electrochem. Commun.*, **46** (2014) 56.

• Non-flammable Electrolyte

Flammability Test and Electrolyte Stability

A1098 Journal of The Electrochemical Society, **164** (6) A1098-A1109 (2017)

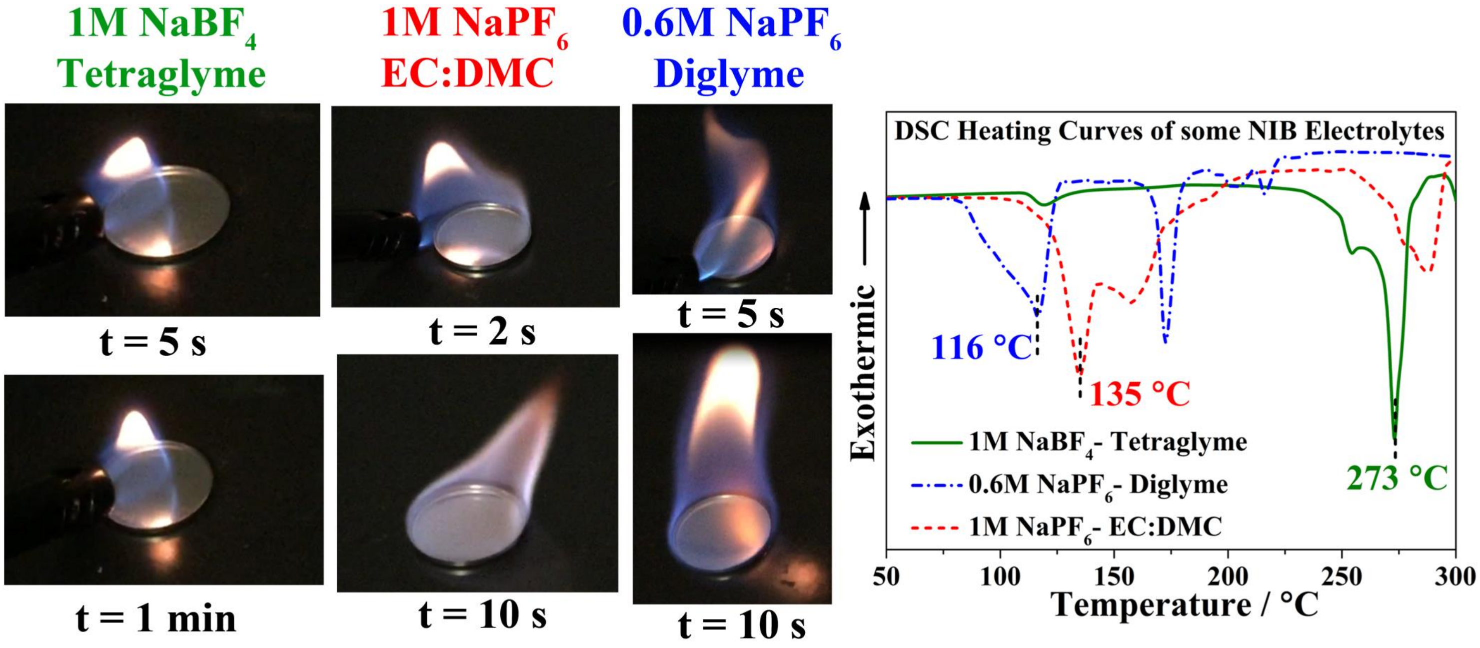
Monoclinic Sodium Iron Hexacyanoferrate Cathode and Non-Flammable Glyme-Based Electrolyte for Inexpensive Sodium-Ion Batteries

Ashish Rudola,[a,b] Kang Du,[a] and Palani Balaya[a,*,z]

[a]Department of Mechanical Engineering, National University of Singapore, 117576, Singapore
[b]Department of Materials Science and Engineering, National University of Singapore, 117575, Singapore

Non-flammable glyme based electrolyte

1M $NaBF_4$ in Tetraglyme did not catch fire even after 1 min of open flame exposure[1]

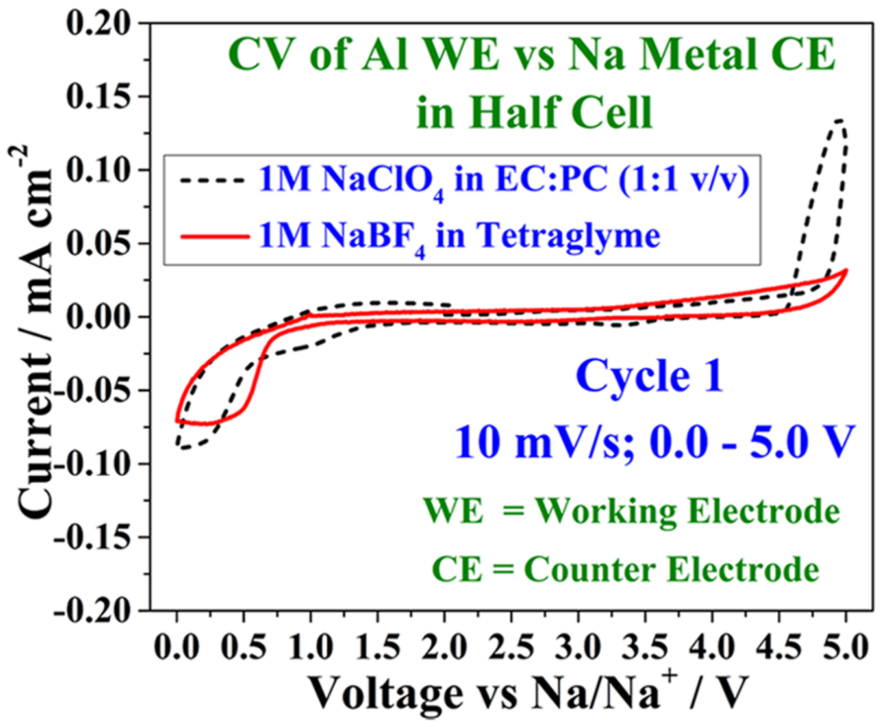


1M $NaBF_4$ in Tetraglyme exhibits high thermal stability

[1]A. Rudola, K. Du and P. Balaya, *J. Electrochem. Soc.*, **164** (2017) A1098

Electrochemical stability window

1M $NaBF_4$ in Tetraglyme: a versatile sodium-ion electrolyte



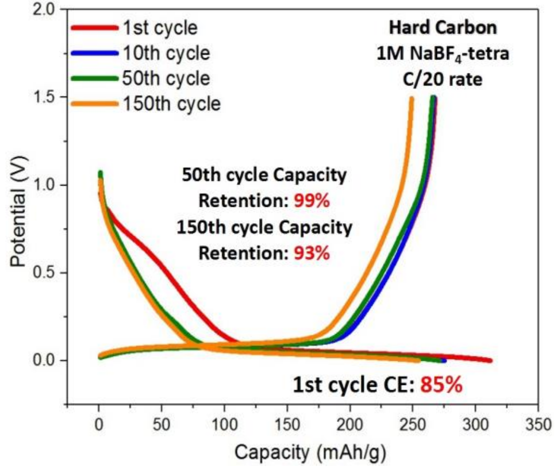
High oxidative and reductive stability → 0.0 - ≈ 4.5 V *vs* Na/Na^+

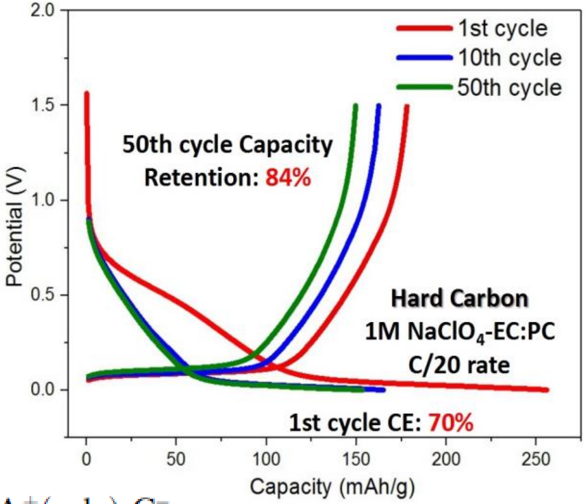
High oxidative stability (> 4 V *vs* Na/Na^+) is unusual for glyme-based electrolytes

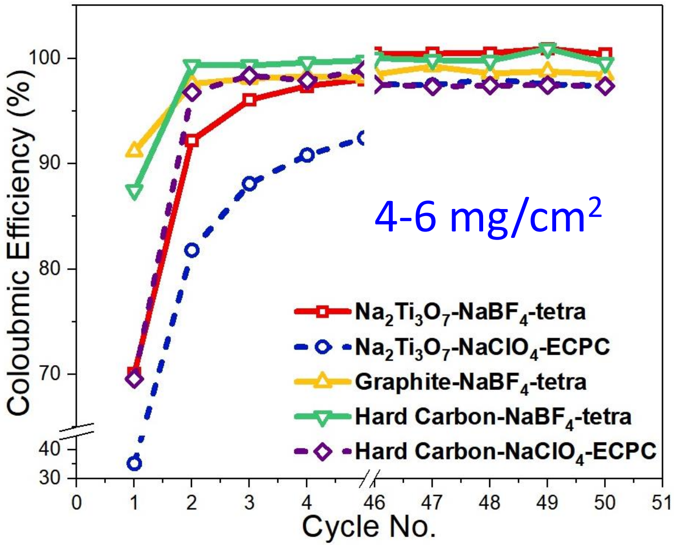
Being glyme-based, this electrolyte causes reliable and non-dendritic cycling of Na CE with little passivation layer

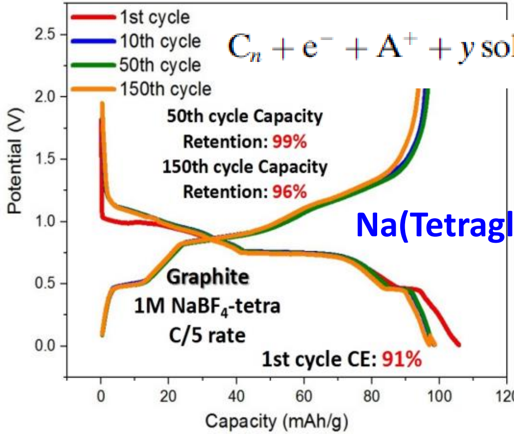
Conductivity not as high as 1M $NaClO_4$ (≈4.4mS/cm), but acceptable (1.3 mS/cm).

Cycling performance of Hard Carbon and Graphite: 1M $NaBF_4$-Tetraglyme *vs* 1M $NaClO_4$-EC:PC









$$C_n + e^- + A^+ + y\,\mathrm{solv} \rightleftharpoons A^+(\mathrm{solv})_y C^-_n$$

$Na(Tetraglyme)_yC_n$

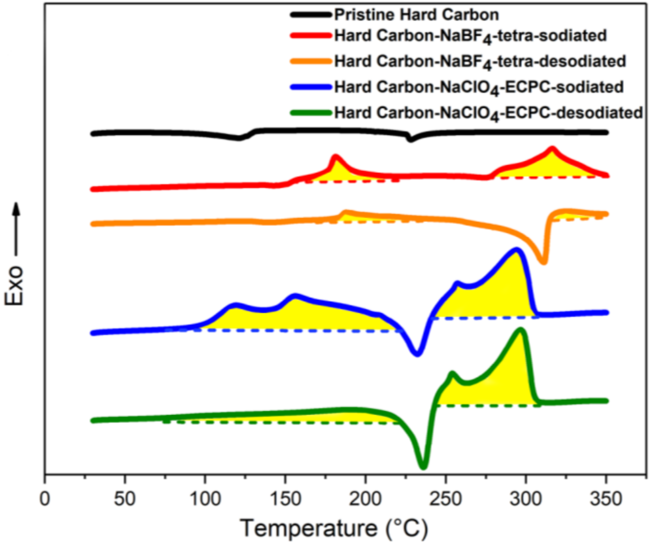
Solvated Na: co-intercalation[1-2]

Compared to **1M $NaClO_4$-EC:PC** electrolyte, all cells tested using **1M $NaBF_4$-Tetraglyme** delivered:

- **High first cycle coloumbic efficiencies**
- **Stable cycling performances**

[1] B. Jache and P. Adelhelm, *Angew. Chemie - Int. Ed.* **53** (2014) 10169
[2] H. Kim….K. Kang, *Adv. Funct. Mater.*, **25** (2015) 534.

DSC analysis of Hard Carbon



Binder-free samples; No air exposure

Exothermic peaks are the signs of cracking of the solid-electrolyte interphase (SEI)[1]

Energy released (J/g) - calculated by the yellow shaded parts

1st onset T for 1M $NaBF_4$-Tetraglyme cells much higher (safer) than 1M $NaClO_4$-EC:PC

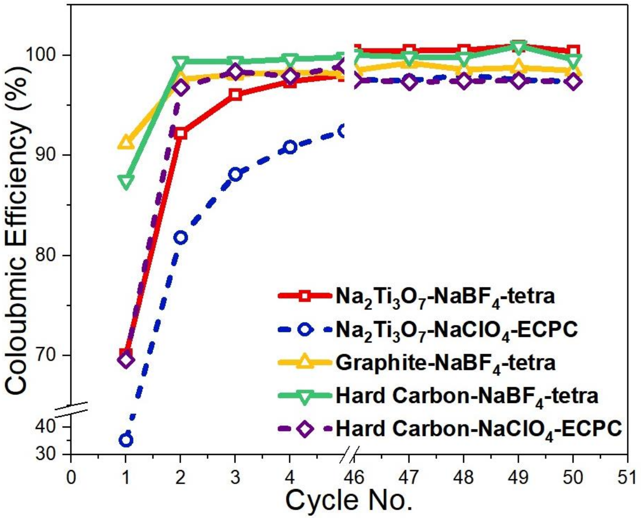
Unit energy released for 1M $NaBF_4$-Tetraglyme cells much lower (safer)

Thermally stable surface layer (SEI) with 1M $NaBF_4$ in Tetraglyme

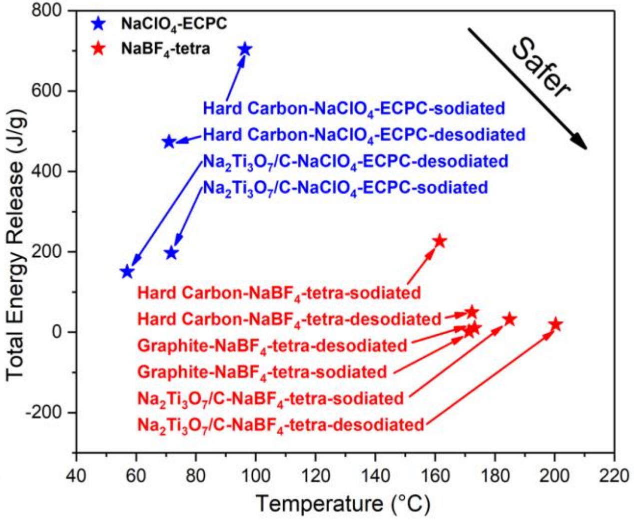
Sample	1st Onset T (ºC)	1st Offset T (ºC)	1st Energy released (J/g)	2nd Onset T (ºC)	2nd Offset T (ºC)	2nd Energy released (J/g)	Total Energy Released (J/g)
$NaBF_4$-Tetraglyme:Sodiated	161.5	243.3	84.2	278.3	351.1	152.9	237.1
$NaBF_4$-Tetraglyme:Desodiated	172.3	237.8	32.3	315.4	350.4	17.0	49.2
$NaClO_4$-EC:PC:Sodiated	96.4	220.9	358.8	242.6	308.2	345.0	703.8
$NaClO_4$-EC:PC:Desodiated	103.8	216.7	75.9	224.2	308.1	346.8	422.7

Further investigations on SEI

Cycling



DSC



1M $NaBF_4$-Tetraglyme delivers significant higher first cycle coulombic efficiencies than 1M $NaClO_4$-EC:PC

Unit energy released for 1M $NaBF_4$-Tetraglyme cells much lower (safer) than 1M $NaClO_4$-EC:PC[1]

The formation of passivation layers (SEI) on the anodes can be a major contributor to the lower coulombic efficiency of the first cycle[1]

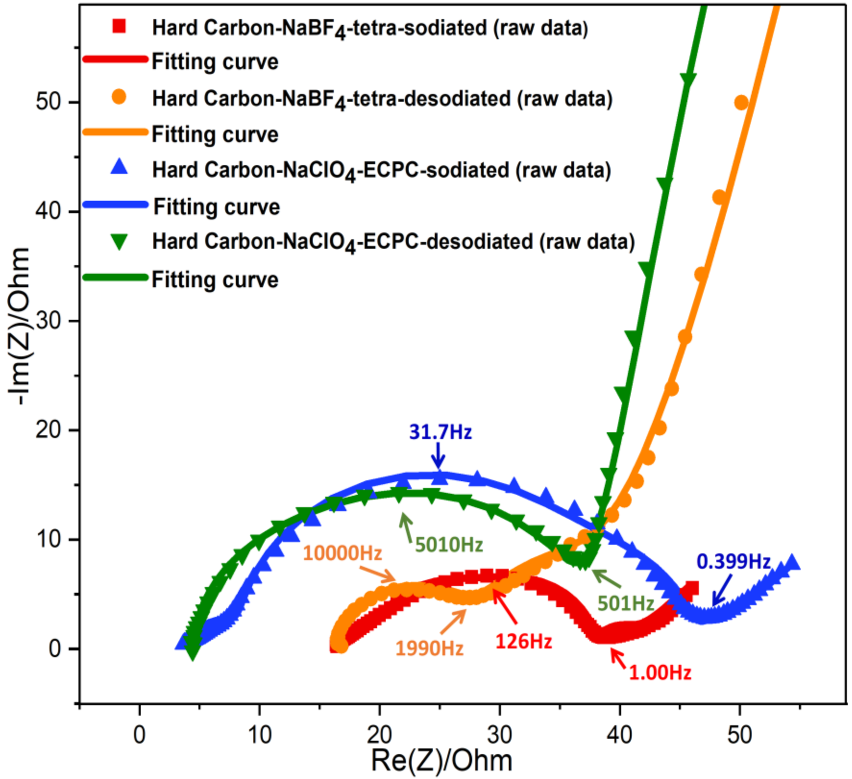
Exothermic peaks are the signs of cracking of the solid-electrolyte interphase (SEI)[2]

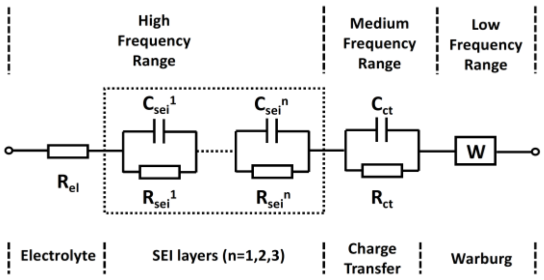
Further investigations on SEI

[1] M. Winter and J. O. Besenhard in Handbook of Battery Materials (2nd Ed), Wiley **2011**.

[2] A. Ponrouch….M.R. Palacin, *Energy. Environ. Sci.*, **5** (2012) 8572.

EIS analysis of Hard Carbon symmetric cells





To eliminate the contribution from the Na metal, symmetric cells were used[1,2]

Cells cycled in 1M $NaBF_4$-Tetraglyme shows smaller semicircles at high frequency range[3](SEI) than 1M $NaClO_4$-EC:PC

The semicircles at high frequency range (SEI) shrink after the desodiation process

Stable & less resistive SEI layer is formed using glyme based electrolyte

[1] K. Du…P. Balaya, *Energy Storage Mater.*, **29** (2020) 287

[2] J. Y. Song…C.C. Wan, *J. Power Sources*, **111** (2002) 255

[3] M. D. Levi and D. Aurbach, *J. Phys. Chem. B.*, **101** (1997) 4630.

• $Na_3V_2(PO_4)_3$ cathode

Energy Storage Materials 29 (2020) 287–299

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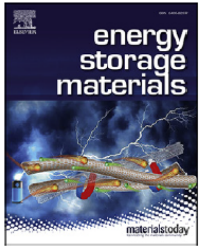
journal homepage: www.elsevier.com/locate/ensm

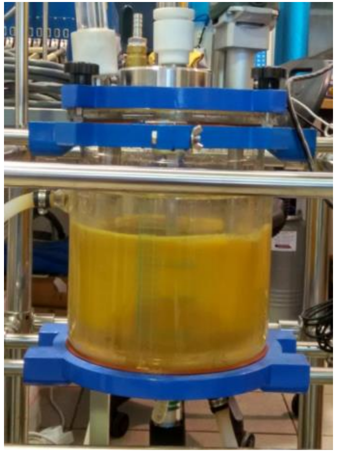


A comprehensive study on the electrolyte, anode and cathode for developing commercial type non-flammable sodium-ion battery

Kang Du [1], Chen Wang, Lihil Uthpala Subasinghe, Satyanarayana Reddy Gajella, Markas Law [1], Ashish Rudola, Palani Balaya [*]

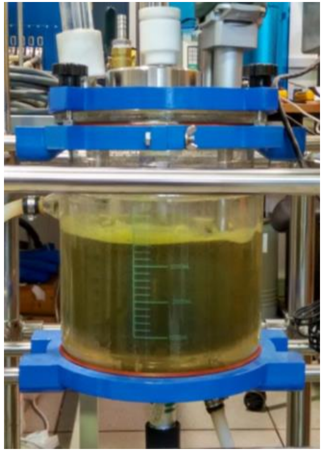
Department of Mechanical Engineering, National University of Singapore, 117575, Singapore

Synthesis of Zn doped $Na_3V_2(PO_4)_3$



Stirring

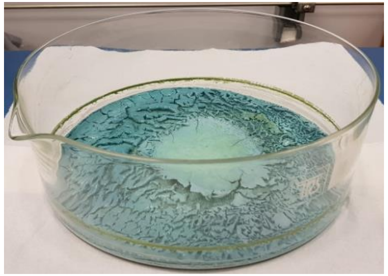
24 h



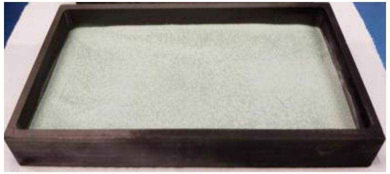
Water-rich synthesis

Drying

24 h

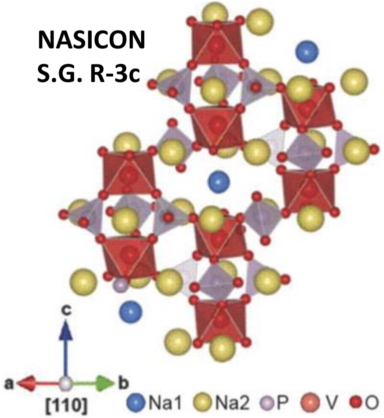


After drying



Pre-calcination

Post-calcination (0.5kg yield)

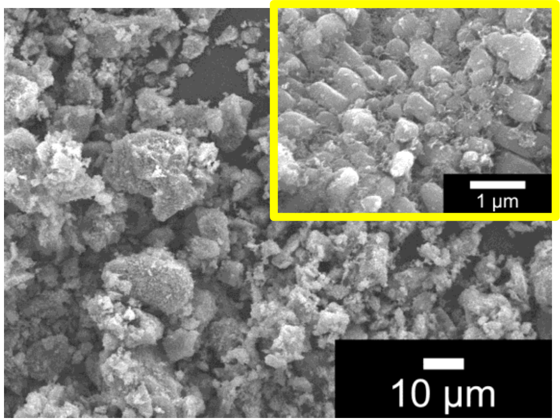


Rhombohedral structure

K. Saravanan,...P. Balaya, Adv. Energy Mater. **3** (2013) 444

Materials characterization

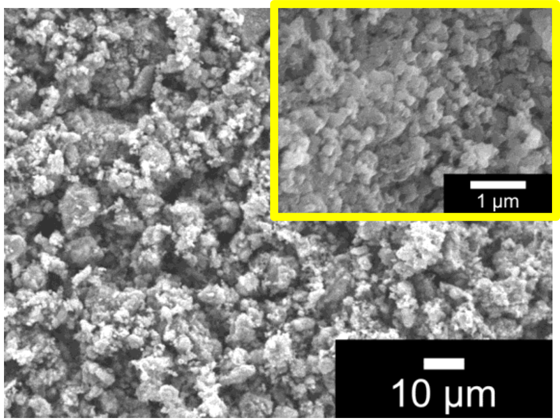
Pristine $Na_3V_2(PO_4)_3$



Primary particle size: 200-800 nm

Secondary particle size = 5-15 μm

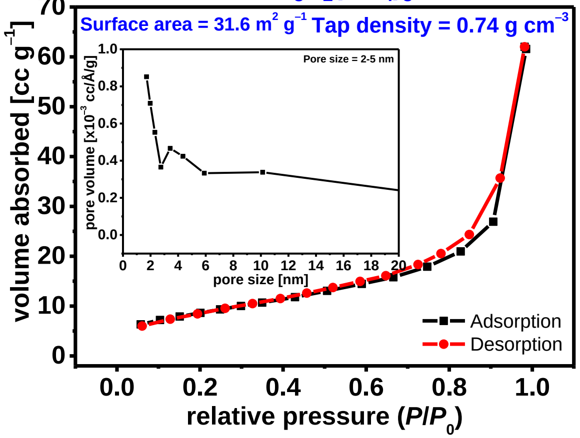
Modified $Na_3V_2(PO_4)_3$



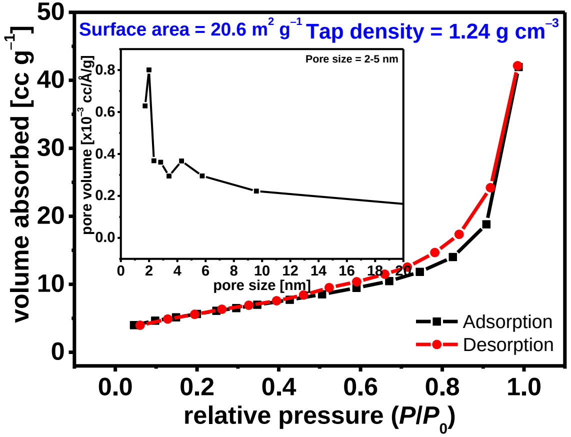
Primary particle size: 100-200 nm

Secondary particle size = 5-10 μm

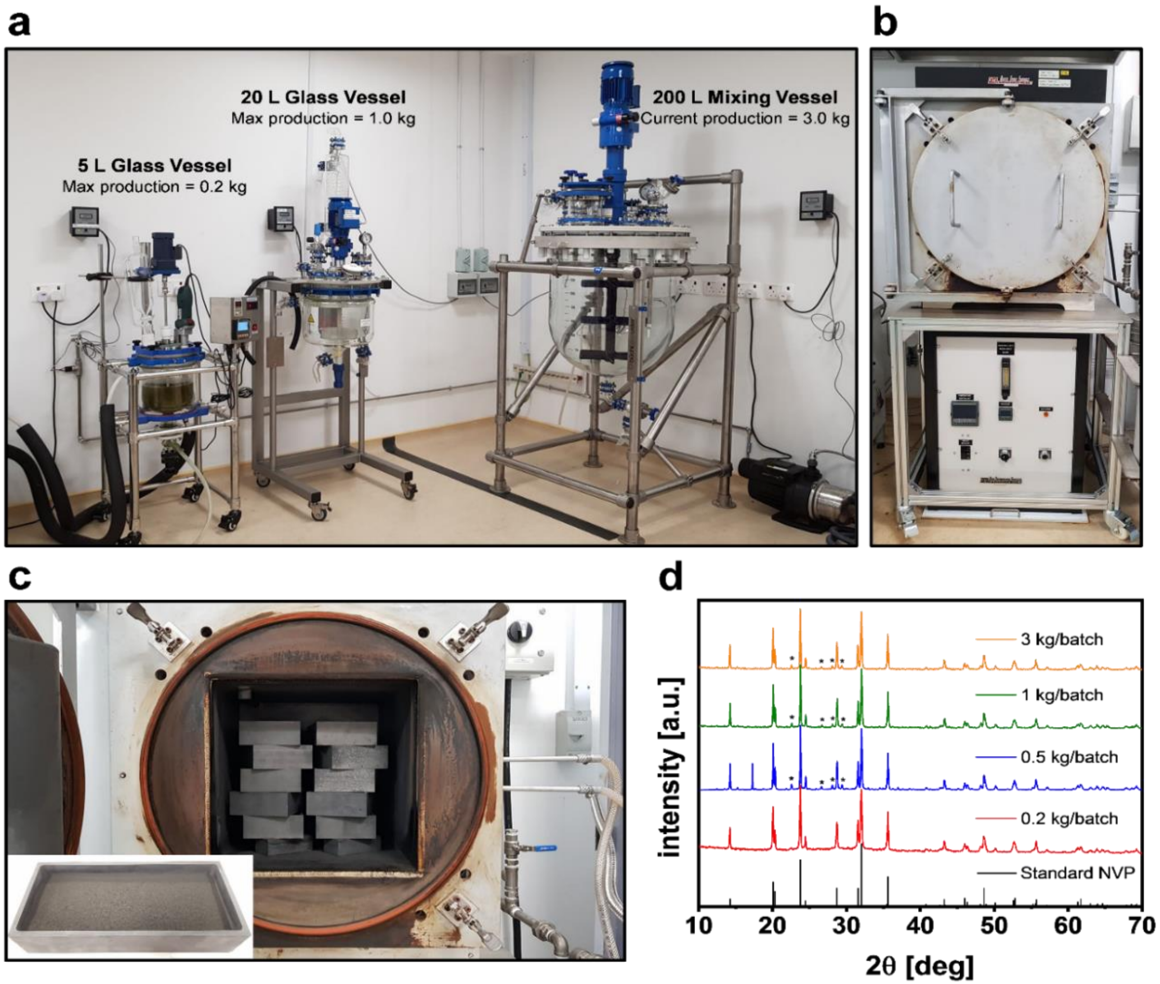
Pristine $Na_3V_2(PO_4)_3$



Zn-doped $Na_3V_2(PO_4)_3$



Kilo-scale synthesis: Zn doped $Na_3V_2(PO_4)_3$ cathode material



Prototype line @ NUS for 18650 and pouch cells (20% and 1% dry rooms)


Slurry mixer


Coating machine

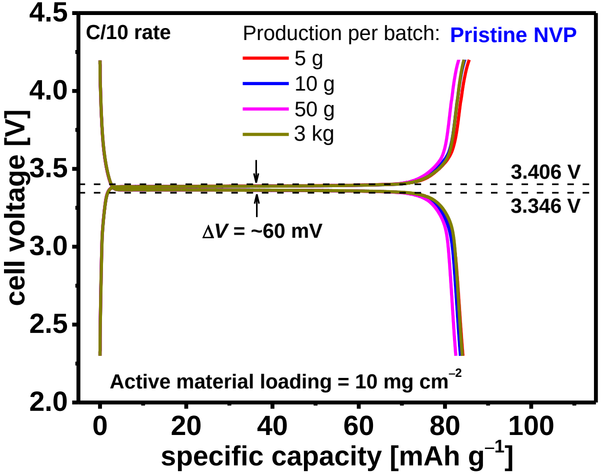

Twin-roller press

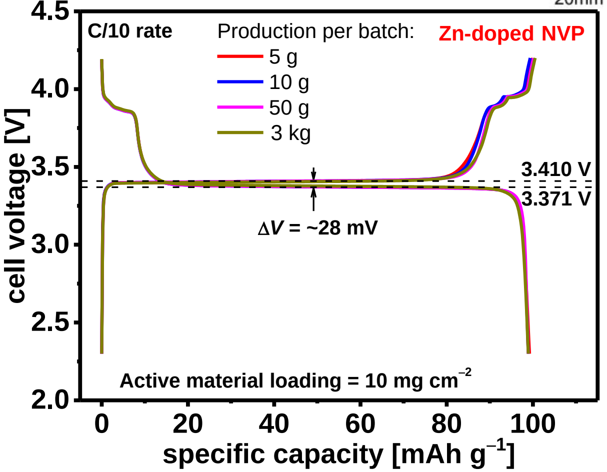

Semi-automatic winding

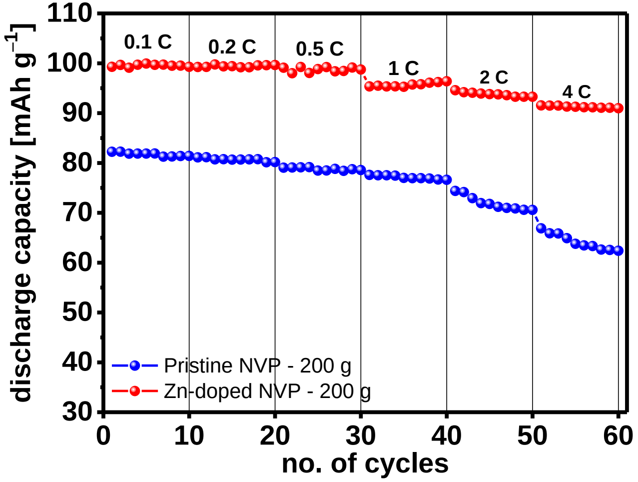

Glove box to fill electrolyte and crimping


18650 cell

$Na_3V_2(PO_4)_3$ *vs.* Sodium half-cell

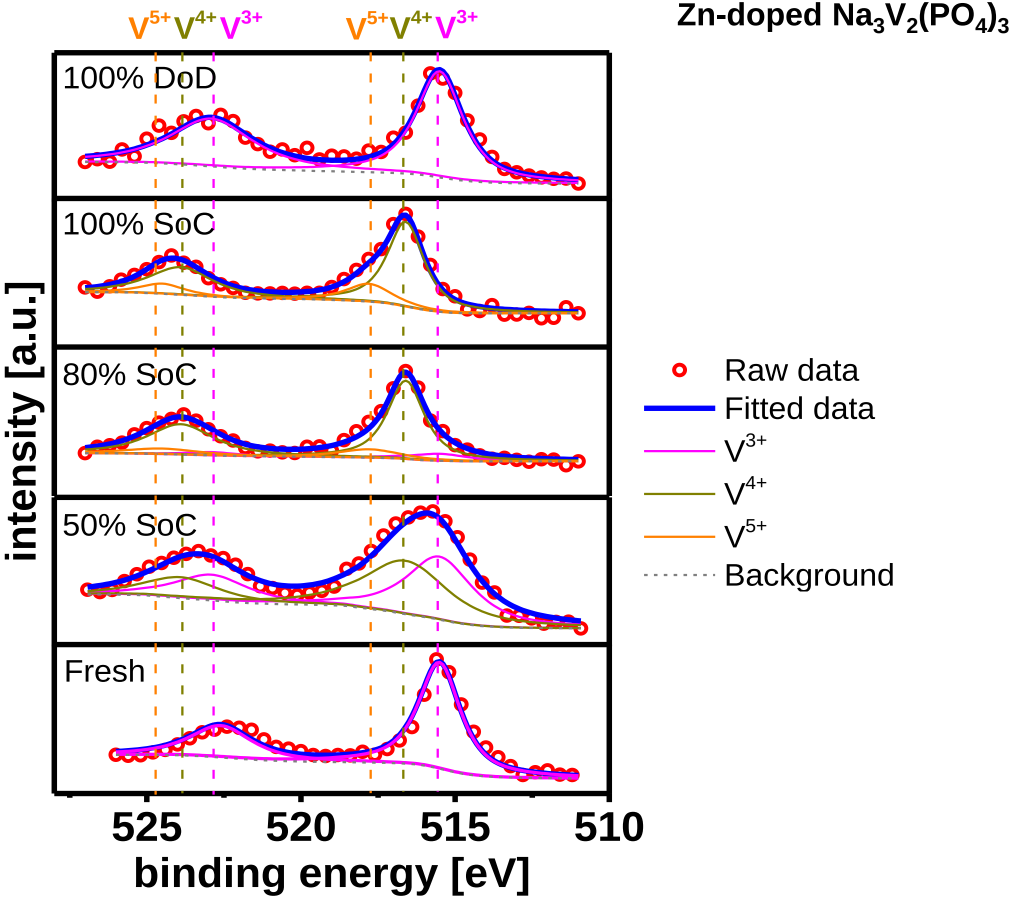






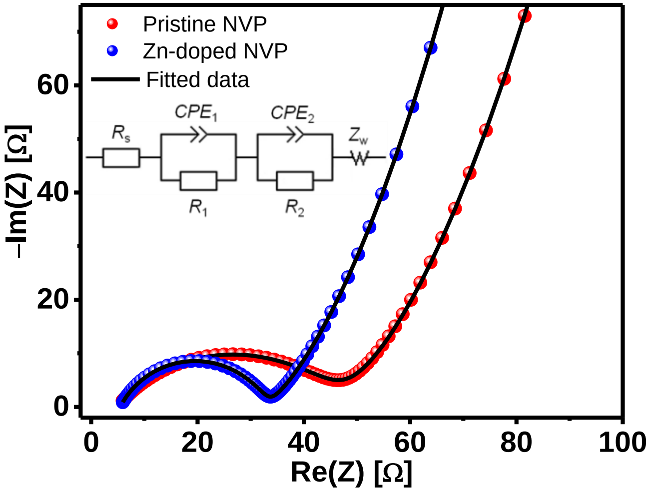
Current rate	1st cycle discharge capacity [mAh g^{-1}]	
	Pristine NVP	Zn-doped NVP
C/10	81.9	99.2
C/5	80.5	99.3
C/2	78.9	98.8
1 C	77.6	95.2
2 C	74.3	93.6
4 C	66.8	91.1

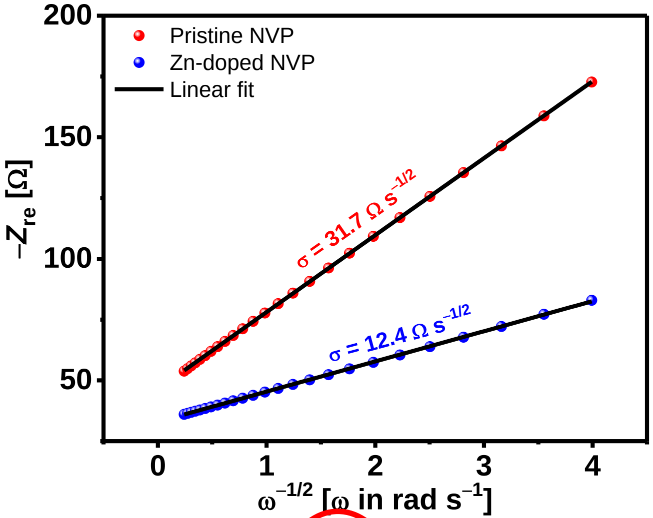
Redox reaction of Vanadium in NVP: XPS studies



Redox activity of $V^{4+} \rightarrow V^{5+}$ is detected at 80% SoC during charge; At 100% SoC, all V^{3+} is utilized.

Diffusion analysis with three-electrode cell





Sample	R_s [Ω]	R_1 [Ω]	R_2 [Ω]
Pristine NVP	4.73	9.41	41.2
Zn-doped NVP	5.45	8.14	20.6

Sample	D_{Na} [×10^{-16} cm^2 s^{-1}]
Pristine NVP	2.93
Zn-doped NVP	19.2 ↑ 1 order

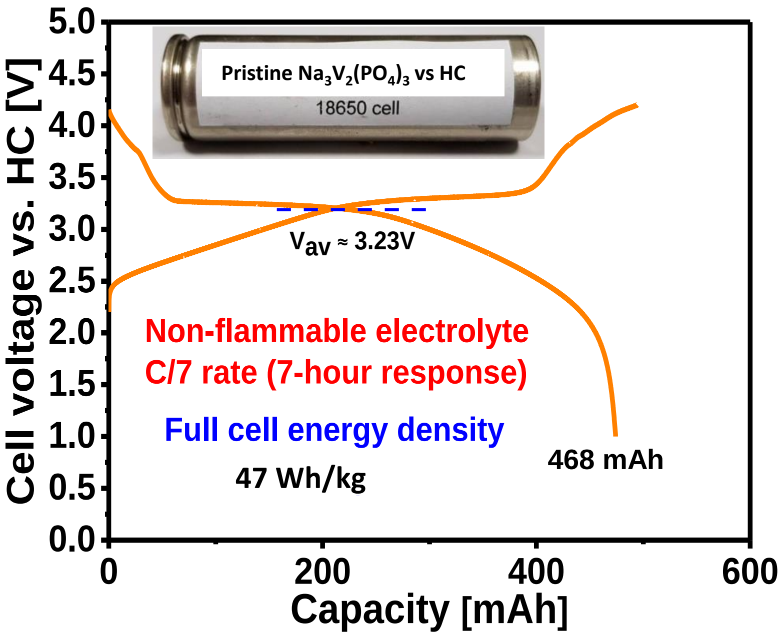
R_s = Solution and contacts resistance

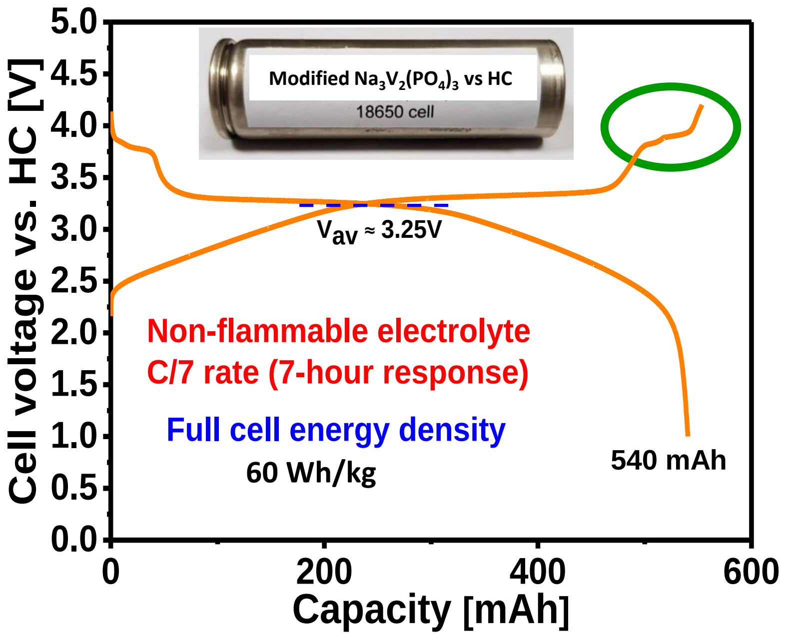
R_1 = Passivation film resistance

R_2 = Charge transfer resistance

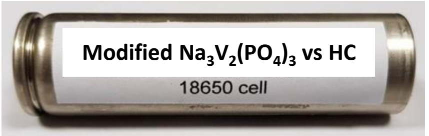
Na diffusion coefficient of Zn-doped NVP is almost **1 order of magnitude higher** than Pristine NVP

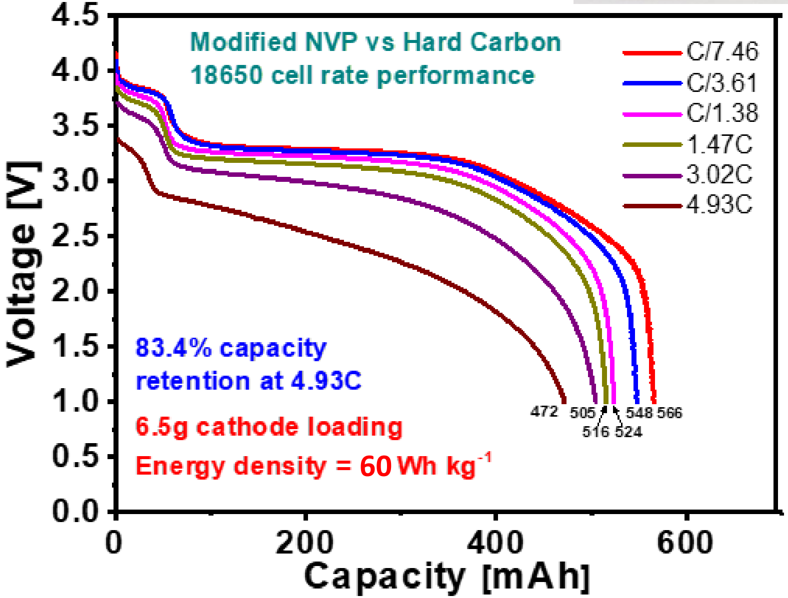
$Na_3V_2(PO_4)_3$ *vs*. Hard Carbon full cells

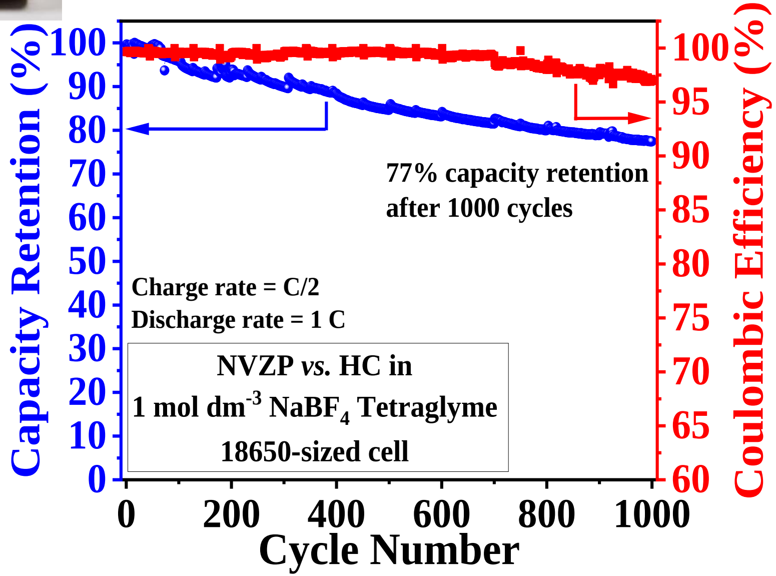




$Na_3V_2(PO_4)_3$ cathode vs Hard Carbon anode





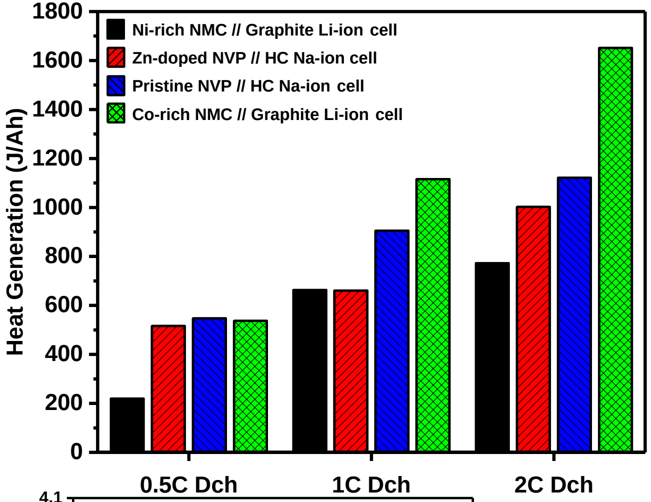


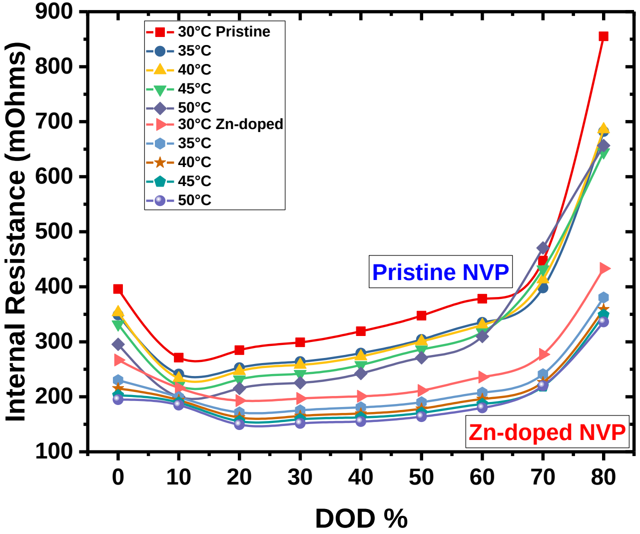
L.U. Subasinghe (2020, NUS Thesis)

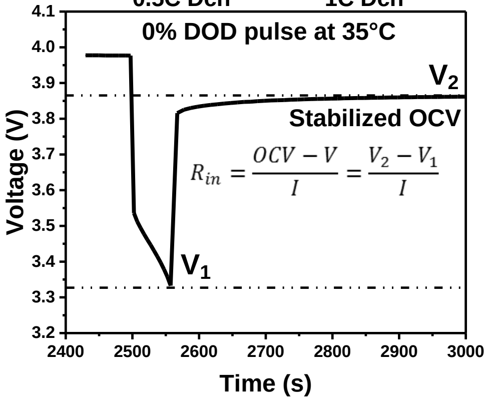
Capacity retention: 77% after 1000 cycles (**100% DOD**)

Future R&D: Energy density: 200 Wh/kg; Cycle life: 5000

Heat generation and internal resistance variation of NVP vs. Hard Carbon 18650 cells







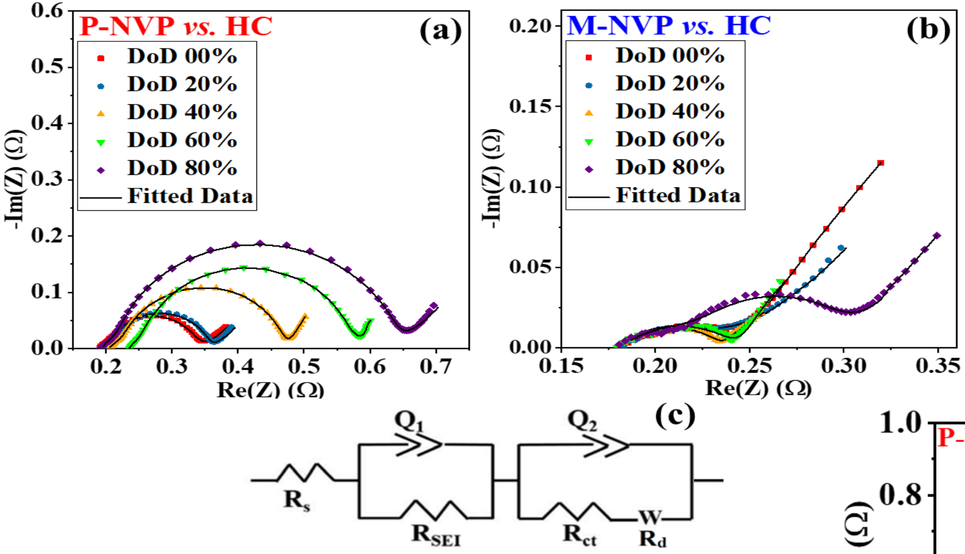
Temperature (°C)		30	35	40	45	50
Average Internal Resistance (mΩ)	Pristine	400	345	344	329	321
	Zn-doped	248	220	207	199	193

Zn-doped cell has shown a lower internal resistance than pristine cell at any DOD/ at any temperature

L.U. Subasinghe (2020, NUS Thesis)

B. Manikandan, C. Yap, and P. Balaya, *J. Electrochem. Soc.*, 164 (2017) A2794.

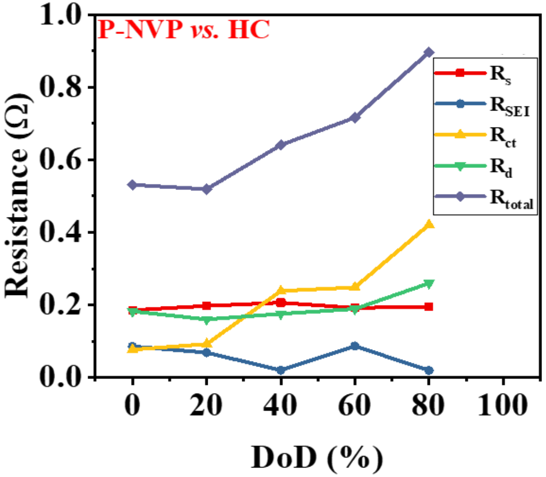
Individual components of internal resistance of $Na_3V_2(PO_4)_3$ *vs.* Hard Carbon 18650 cells

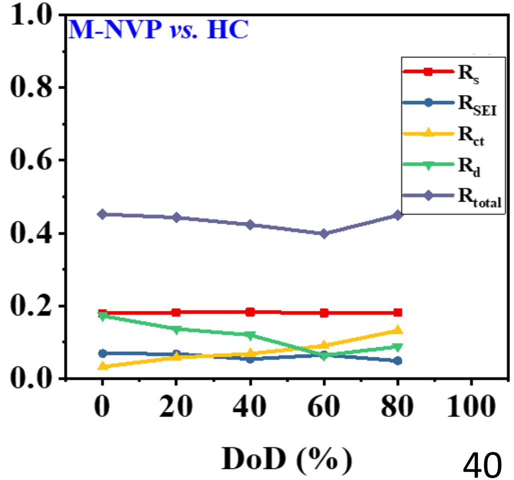


Charge transfer resistance is the most limiting factor

Zn doping in NVP:

- Reduces charge transfer resistance
- Improve Na chemical diffusion





- R_s = Solution Resistance
- R_{SEI} = Solid-electrolyte interphase resistance
- R_{ct} = Charge transfer resistance
- R_d = Diffusion resistance

L.U. Subasinghe (2020, NUS Thesis)

• O3 type Na-layered oxides

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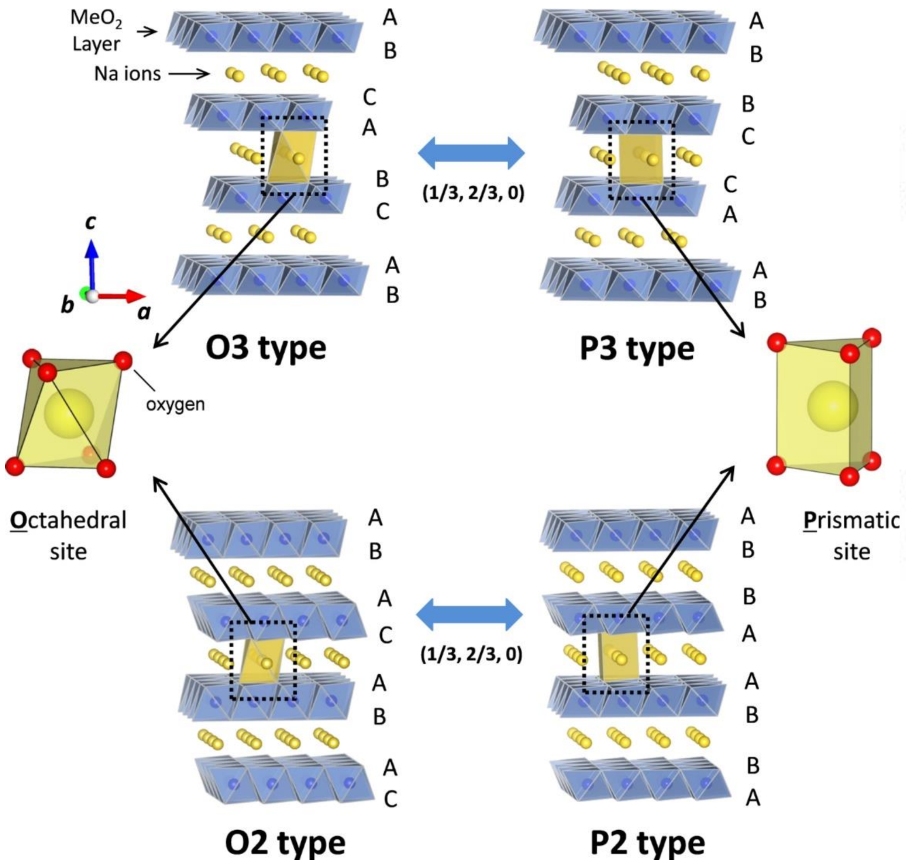
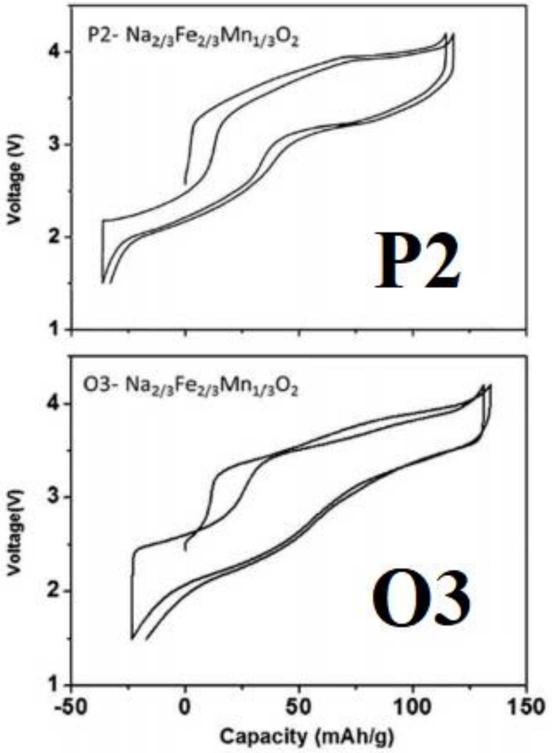
Cite this: *J. Mater. Chem. A*, 2019, 7, 25944

Developing an O3 type layered oxide cathode and its application in 18650 commercial type Na-ion batteries†

Abhinav Tripathi,[a] Ashish Rudola,[a] Satyanarayana Reddy Gajjela,[a] Shibo Xi[b] and Palani Balaya*[a]

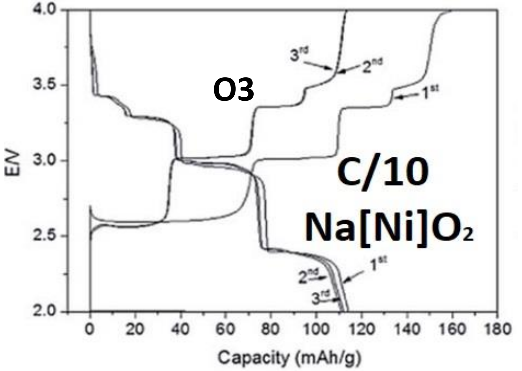
Oxides as cathode for Na-ion battery

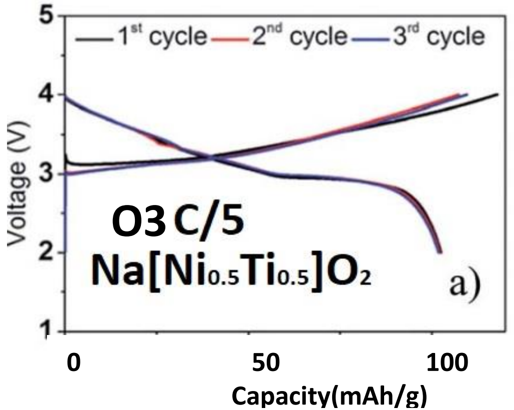


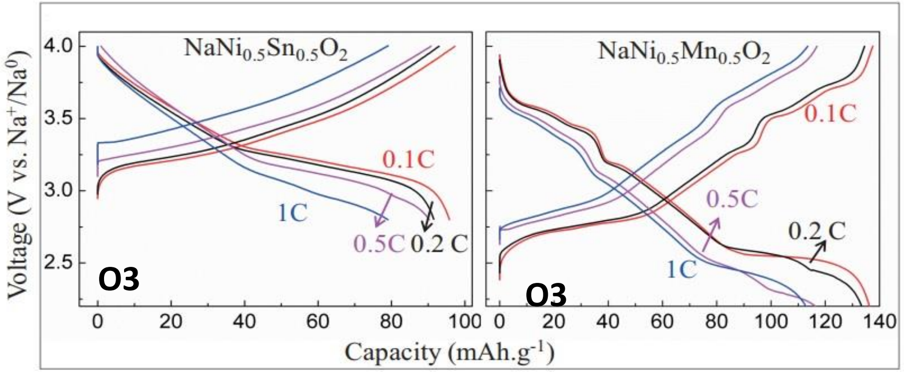


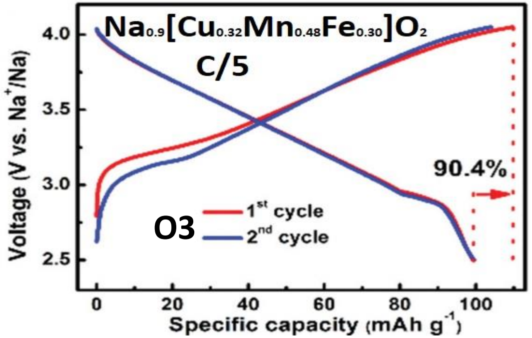
C. Delmas, C. Fouassier, P. Hagenmuller, *Physica B+C*, **9** (1980) 81
N. Yabuuchi and S. Komaba, *Sci. and Tech. of Adv. Mat.*, **15** (2014) 4.

Overview : Sodium Layered Oxides (O3-Type)









Sodium layered oxides - generally not air stable; performance mitigate if exposed to H_2O, CO_2 etc. Use of water-based binders won't be possible if active material is not stable in water.

1. K. Kubota…S. Komaba, *MRS Bulletin,* **39** (2014) 416; **2.** M. H. Han…T. Rojo, J. Power Sources, 258 (2014) 266;
3. H. Yu…H. Zhou, Chem. Commun.,, 50 (2014) 457; **4.** M. Sathiya…J.M. Tarascon, Adv. Energy Mater., 8 (2018), 1702599;
5. L. Mu….X. Huang, Adv. Mater. 27 (2015) 6928.

GEN 1 - $Na_{0.9}Cu_{0.22}Mn_{0.48}Fe_{0.30}O_2$

GEN 2 - $Na_{0.9}Cu_{0.22}Mn_{0.43}Fe_{0.30}Ti_{0.05}O_2$

GEN 3 - $Na_{0.9}Cu_{0.12}Ni_{0.10}Mn_{0.43}Fe_{0.30}Ti_{0.05}O_2$

Water based synthesis and binder

- Precursors used for Na, Mn, Fe, Cu, Ti and Ni are $NaCO_3$, $MnCO_3$, $Fe(Ac)_2$, $Cu(Ac)_2$, Ti(Ipr) and $Ni(Ac)_2$ respectively.
- These precursors were mixed in stoichiometric amounts in milli-Q water.
- After homogenous mixing, the solution was dried and calcined in air at 900 ^{o}C for 10h.
- For electrode preparation, water based slurry of Na-oxide, CMC powder, and Super P was prepared in the ratio 85:5:10 respectively.

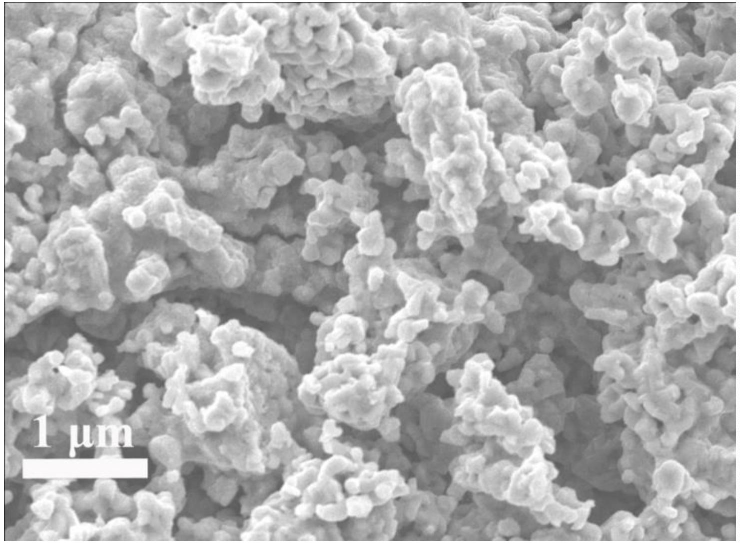
Ex-situ XANES and EXAFS Analyses

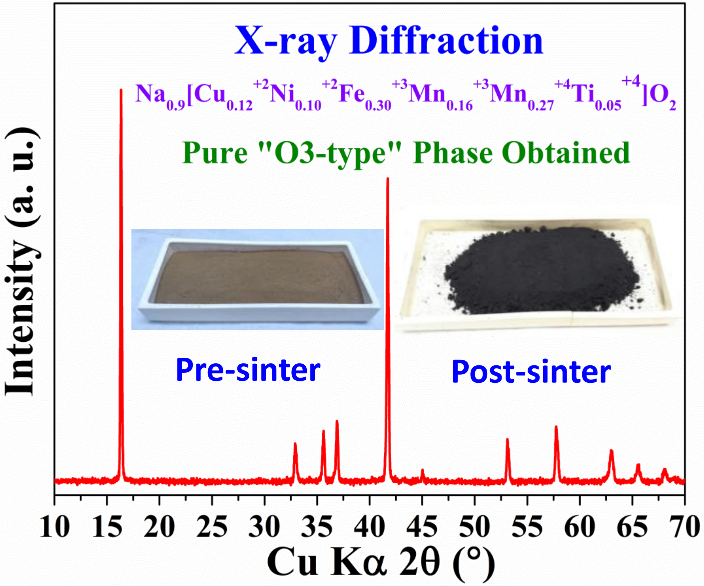
L. Mu....X. Huang, Adv. Mater. 27 (2015) 6928.

GEN 3 - $Na_{0.9}Cu_{0.12}Ni_{0.10}Mn_{0.43}Fe_{0.30}Ti_{0.05}O_2$

$Na_{0.9}[Cu_{0.12}^{+2} Ni_{0.10}^{+2}Fe_{0.30}^{+3}Mn_{0.16}^{+3}Mn_{0.27}^{+4} Ti_{0.05}^{+4}]O_2$

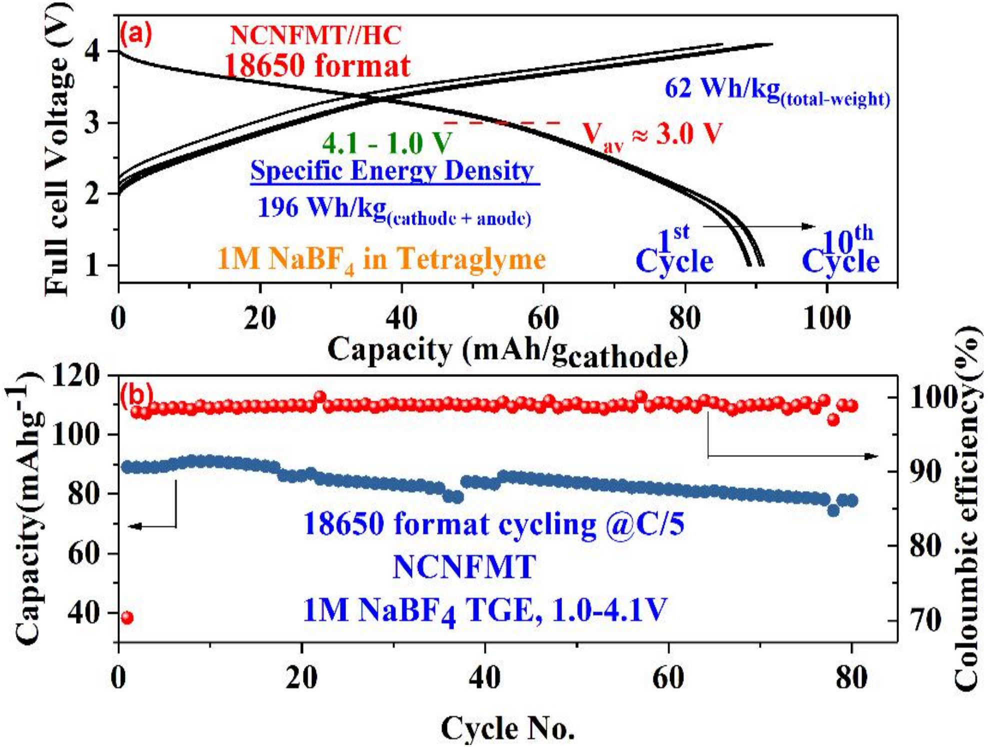
Devised water-based synthesis → Scaled-up to 100 g/batch





18650 Cell: O3 oxide *vs.* Hard Carbon

Energy density = 62 Wh/kg



Take Home Message

Non-flammable

Low cost

High oxidative stability

Stable cycling performance

$Na_3V_2(PO_4)_3$/ Hard Carbon Graphite

Ether-based electrolyte: 1M $NaBF_4$ in Tetraglyme

High safety level

DSC results: High 1st onset temperature and low unit energy released

High 1st cycle coulombic efficiency

Compared with carbonate-based electrolyte: 1M $NaClO_4$-EC:PC

Thin/less SEI formation

DSC, EIS and ATR-FTIR results

Compared with carbonate-based electrolyte: 1M $NaClO_4$-EC:PC

(i) Na_2MnSiO_4

(ii) $Na_3V_2(PO_4)_3$ *vs*. Hard Carbon

(iii) O3 - $Na_{0.9}Cu_{0.12}Ni_{0.10}Mn_{0.43}Fe_{0.30}Ti_{0.05}O_2$ *vs*. Hard Carbon

Acknowledgement

- Markas Law, Ashish Rudola, Abhinav Tripathi, Du Kang, Lihil U. Subasinghe, Wang Chen, K. Saravanan, Balasundaram Manikandan, Satyanaraya Reddy Gajjela, Doron Aurbach and Joachim Maier

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- National University of Singapore

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Thank you for your time.

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Presenter	**Dr. Palani Balaya** mpepb@nus.edu.sg

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