11-30-2023

Sodium-ion Battery Projects Overview
DOE Vehicles Technology Office (VTO)

Christopher Johnson

NAATBatt Sodium & Zinc Conference
11-30-2023 to 12-1-2023
Houston, Texas, USA

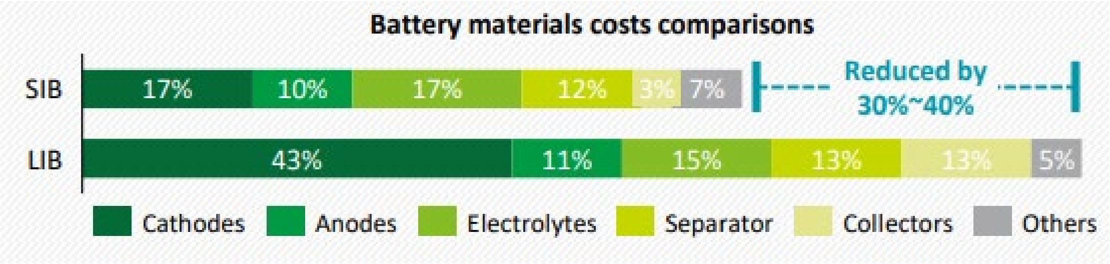
U.S. DEPARTMENT OF ENERGY
Argonne National Laboratory is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC.

Content Source: DOE VTO BMR Annual reports

Sodium-Ion Batteries

- Low-cost, sustainable complement to LIB
  - No Li, Co; Low-to-no Ni
  - Al current collector on both sides
  - ~60-70% of LFP cost
- High power possible >15C
- Safety (less flammable, explosive and not corrosive)
- Zero-volt de-energization (transportation regulation)
- Similar chemistry allows leveraging LIB technology
- Inherently lower energy than LIB drives more stringent cost targets for SIBs
  - Short-range cost-effective BEVs
- Employing economical materials (Na, Mn, Fe, Al), must be complemented by developing a new low-cost manufacturing processes

		Li-ion	Na-ion
Resources	Abundance (ppm in the cortex)	Li (20)	Na (23600)
	Distribution	93% in South America, China and Australia	Worldwide
	Toxicity	Co	Non toxic
	Critical materials (%)	50-60 (Li, Co, Ni)	< 5 (Na, Mn, Fe)
Current collector	Anode	Cu	Al
	Catode	Al	Al

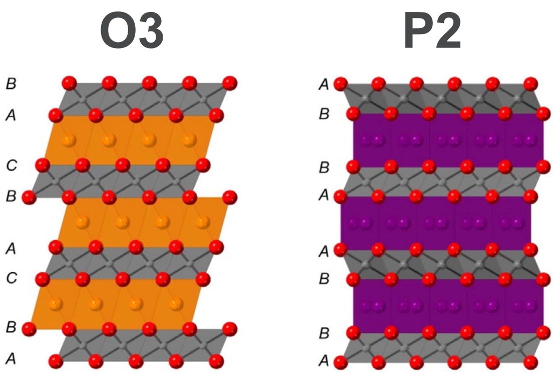
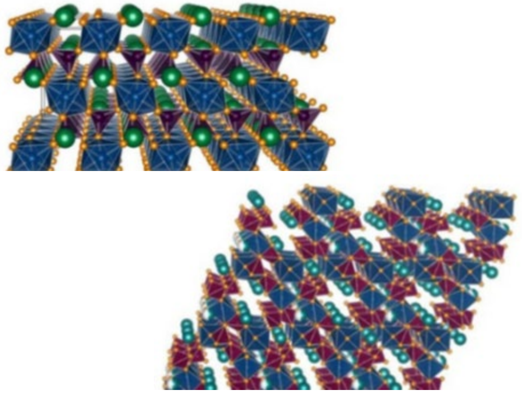
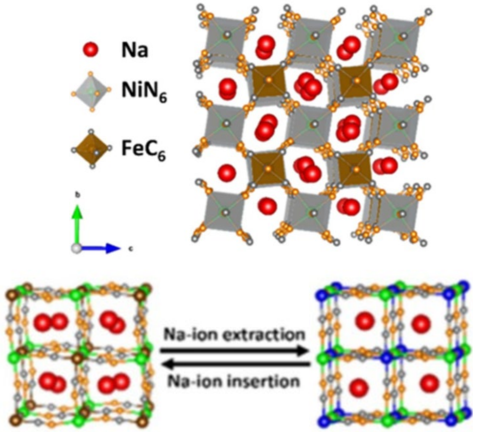


Performance Benchmarks

	Lead Acid	NiMH	Na-ion	LFP (LMFP)	NMC
Cell specific energy [Wh/Kg]	30-35	45-55	**160**	200 (240)	290
Cell volumetric energy [Wh/L]	100	185	**280**	400 (525)	835
Nominal voltage [V]	2	1.25	**3.1 - 3.2**	3.2 (3.7)	3.6
Cycle Life (80% retention)	200-300	300-500	**>1000**	>1500 - 5000 (1800)	500
Self-discharge [Month]	20%	30%	**5%**	3%	1%

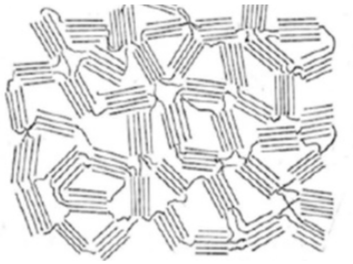
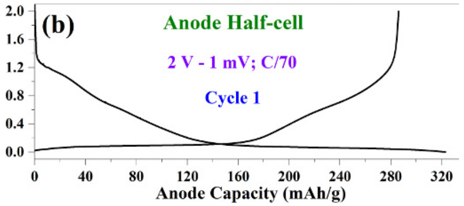
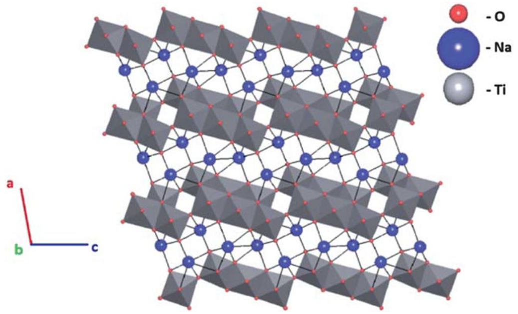
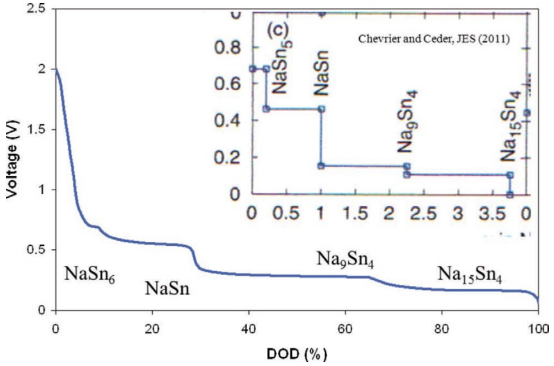
Based on "Sodium Ion (Na-Ion) Battery Market 2023 – "The Next Technology on Battery Mass Production," May 2023, Shmuel De-Leon

Cathodes

Type	Layered oxides	Polyanionic	Prussian blue
	Na_xMO_2	NASICON, NaFP, NVP, NVPF	$Na_xMFe(CN)_6$, etc
			
Pros	• High theoretical capacity (~240 mAh/g) • High energy density • High rate capabiltiy	• Robust structure • Good thermal stability • Cycle stability • Not hygroscopic	• Stable open structure • High reversible capacity • High energy
Cons	• Cycle stability (multiple phase) • Hygroscopic • Low voltage	• Low capacity (~120 mAh/g) • Low energy • Synthesis cost	• Low electronic conductivity (requires large amount of conductive carbon) • Low CE

Anodes

Graphite and Si have negligible sodium storage ability (carbonate electrolytes)

Type	Hard carbon	Ti-based intercalation oxide	Conversion & alloying anodes
	 	TiO_2, $Na_2Ti_3O_7$, etc. 	Sn, Pb, P, Sb, etc. 
Pros	• Current standard anode • Decent specific capacity (~300 mAh/g), voltage, rate performance	• Low working potential (0.3 V for $Na_2Ti_3O_7$)	• High capacity (>500 mAh/g)
Cons	• Limited capacity • Initial irreversible capacity loss • Na plating	• Low electronic conductivity and Li diffusion kinetics • Low capacity	• Large volume change • Low electronic conductivity

Electrolytes

Organic solvents

- Carbonate electrolytes are predominant in current R&D
- Apart from ethylene carbonate (EC)-based solvents, propylene carbonate (PC)-based solvents, which weren’t previously utilized in LIB due to the solvent co-intercalation issue with graphite anodes, are under investigation for their advantages in low-temperature performance
- Novel fluoridated solvents and ionic liquids are being developed as a lab scale

Na-salts

- Early research used $NaClO_4$ salts because battery-grade $NaPF_6$ was not readily available
- At present, battery-grade $NaPF_6$ salt is commercially accessible from Japanese manufacturers
- R&D efforts on new types of Na-salts and local-high-concentrate concepts are ongoing

Manufacturing

Cathodes (Mn-Fe-based layered oxides)

- Similar to Li-CAM synthesis method (co-precipitation and high-temperature calcination)
- Poor morphology, particle density, ambient stability (Mn,Fe oxidative pCAM; hygroscopic CAM) requires process optimization
- Needs for low-cost, eco-friendly alternative synthesis solution

Anodes (Hard carbon)

- High purity HC synthesis from renewable resources (such as sugar, coconut shells) is more expensive than from fossil fuel derivatives (coal, petroleum) due to intensive purification step
- HC production is not currently at scale and the HC materials are not optimized for SIB applications

Electrolytes

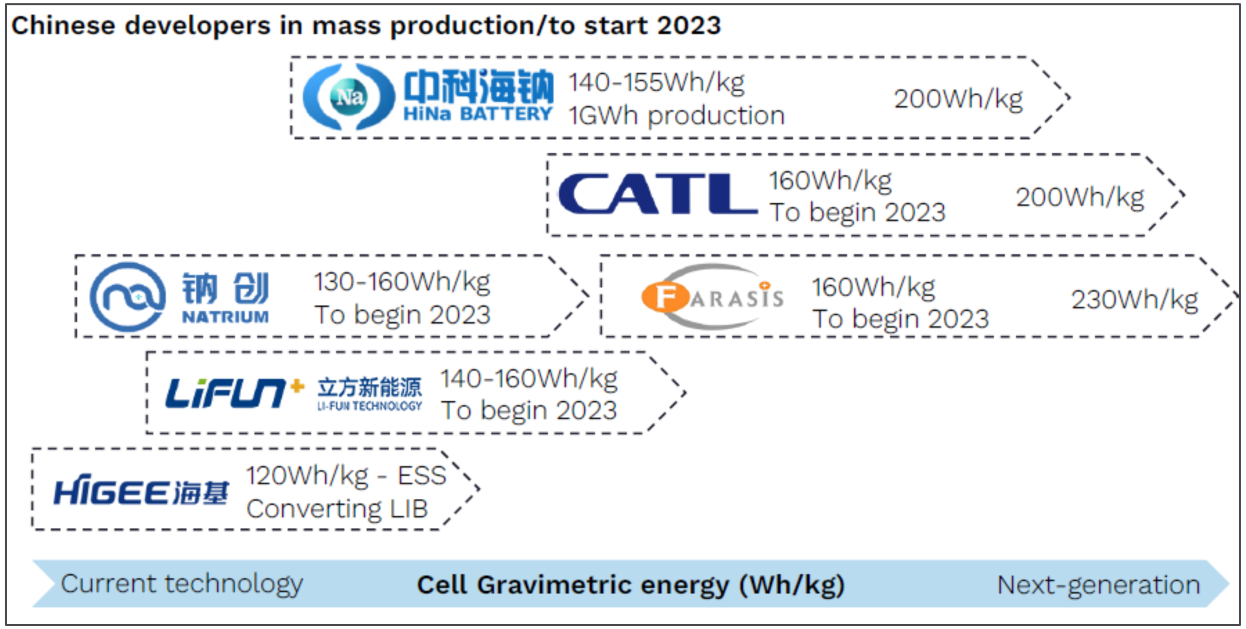
- High purity battery-grade sodium salt ($NaPF_6$) still requires further development to bring cost down

Cell and pack

- Already achieved comparable cell-level energy densities benchmarking the LIB technologies (1st generation SIB cells attained ~160 Wh/kg compared to early LIB at ~80 Wh/kg)
- Further development should focus on higher energy density and better safety
- Thick electrode and cell-to-pack design will significantly boost the pack-level energy density of SIBs (Overall pack density in the range of 140 Wh/kg could be possible with the cell-to-pack design of the 160 Wh/kg cells)

Companies developing/manufacturing SIBs

- China is leading the SIB development
  - China – 27
  - USA – 3 and growing
  - UK – 3 and growing
  - Sweden – 2
  - France – 1
  - Germany – 1
  - Australia – 1
  - Finland – 1
  - Lithuania – 1
  - Bulgaria – 1
  - Japan – 1
  - India – 1



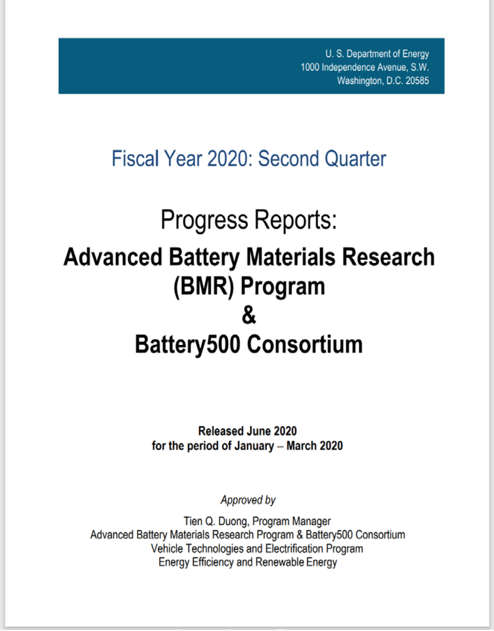
- Chinese companies, such as HiNa, CATL, Farasis, announced mass production plans
- UK-based Faradion and France-based Tiamat have led early development of proto-type SIBs. Faradion, recently acquired by Reliance Industries (India), now announced plans to scale-up.
- US-based Natron Energy is only non-Chinese company announced the engagement in the mass production of sodium batteries. The system is high power non-aqueous sodium batteries based on Prussian blue electrodes.
- Sweden Northvolt PB/HC-based pouch cells with claimed 160 Wh/kg

Based on "Sodium Ion (Na-Ion) Battery Market 2023 – "The Next Technology on Battery Mass Production," May 2023, Shmuel De-Leon, and Rho Motion Emerging Techdnologies report 2023

DOE BMR PROJECTS IN SODIUM-ION

BMR-SIB Projects (FY’22 budget ~ $1.7M)

	ANL	LBNL	PNNL	BNL
Main focus	Oxide cathodes / Alloying Anodes	Oxide anodes	Electrolytes / (New HC anode)	Synchrotron-based characterization
PI	K. Amine / C. Johnson	M. Doeff	Phung M. Le	X.-Q Yang / Enyuan Hu
BMR since	FY19	FY19	FY19	FY14


U. S. Department of Energy
1000 Independence Avenue, S.W.
Washington, D.C. 20585

Fiscal Year 2020: Second Quarter

Progress Reports:
Advanced Battery Materials Research (BMR) Program & Battery500 Consortium

Released June 2020 for the period of January – March 2020

Approved by
Tien Q. Duong, Program Manager
Advanced Battery Materials Research Program & Battery500 Consortium
Vehicle Technologies and Electrification Program
Energy Efficiency and Renewable Energy

https://bmr.lbl.gov/2015-to-present/

BNL – Synchrotron-based characterization

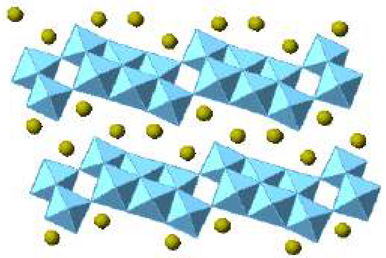
“An exploratory studies of novel sodium-ion battery systems”

- PI: Xiao-Qiang Yang / Eunyuan Hu
- BMR project since FY14
- **Application of synchrotron-based tools to study the sodium-storage and degradation mechanism of cathode materials** (Mostly layered oxides since FY19).
  - In situ and ex situ XRD, hard- and soft- XAS
  - Development of synchrotron-based X-ray imaging techniques: TXM-XANES for 2D valence mapping.
  - Electron-microscopy analysis (3D STEM tomography)
- *Characterized materials*
  - ***FY14 – FY18****:* LTO, $NaCrO_2$, $NaCrS_2$, $Na_{1-x}(Mn,M)O_2$, PB, $Na_3VP_3O_9N$
  - ***FY19 – FY23****:* P2-$Na_{0.72}(Li_{0.24}Mn_{0.76})O_2$, P2-$Na_{0.7}(Mn,Fe,Cu)O_2$, O3-$Na(Mn,Fe,Ni,Co)O_2$, and P3-$Na_{1-x}[Li,Mn,Cu]O_2$ (in collaboration with ORNL)

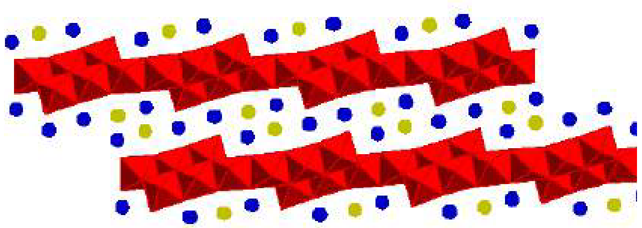
LBNL – Titanates anode materials

"Tailoring high capacity, reversible anodes for sodium-ion batteries"

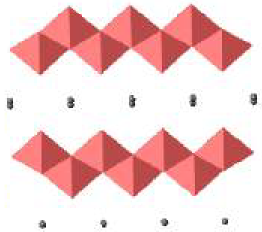
- PI: Marca Doeff
- BMR project since FY19
- Sodium titanate with stepped layered structures
  - Na intercalation operating at low voltage <1.0 V vs. Na
  - Stepped layered structure; property depends on composition and step size
  - High 1st cycle irreversibility; poor cycle property
  - Goal: 200-250 mAh/g with good cycle stability



$Na_2Ti_3O_7$
Step size 3
Flat 0.3V vs. Na
Poor cycle reversibility



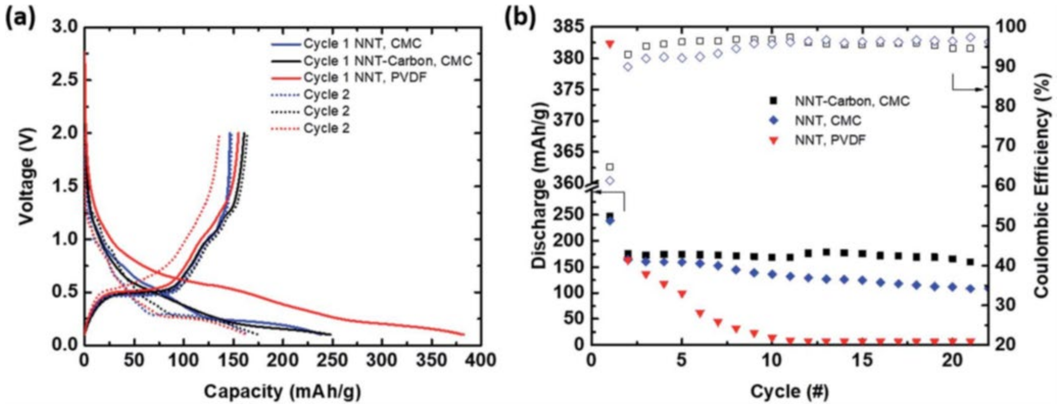
$NaTi_3O_6(OH)$
Sodium nonatitanate (**NNT**; $Na_4Ti_9O_{20}$)
Sloping ~0.3V vs. Na



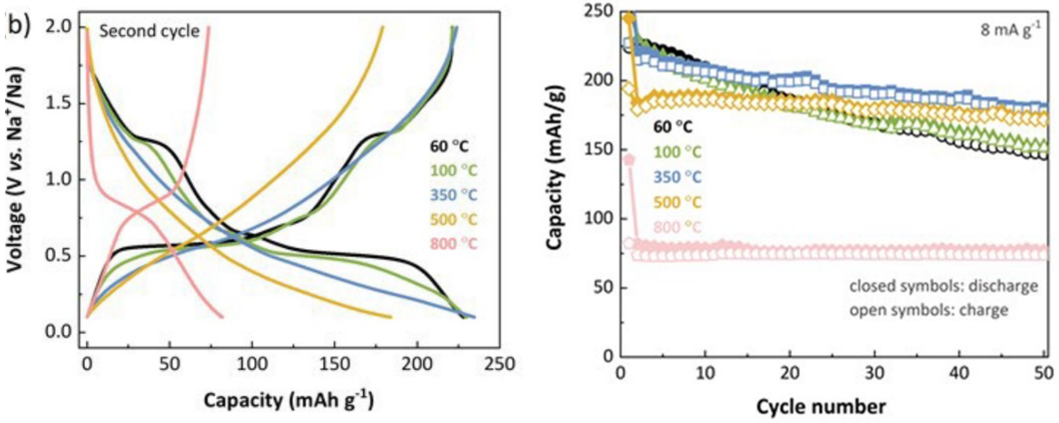
Lepidocrocite, $A_xTi_{2-y}M_yO_4$
(A = K, Rb, Cs; M = Li, Mg, TMs)
Sloping at <1 V vs. Na

LBNL – Titanates anode materials

- FY19-FY20:
  - Optimization of post-annealing of NNT $NaTi_3O_6(OH){\text -}2H_2O$ → $NaTi_3O_6(OH)$ → $Na_2Ti_6O_{13}$ Tunnel → $Na_2Ti_3O_7$
  - Performance improvement by carbon coating and CMC binder



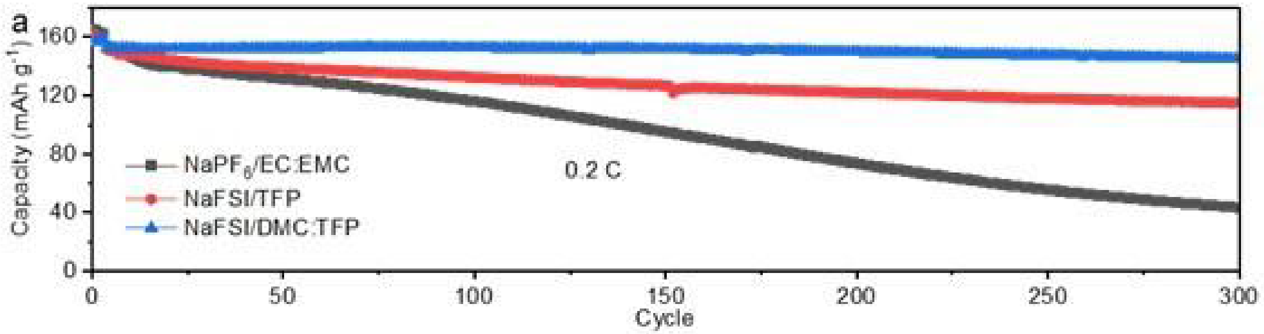
- FY20-FY23:
  - Lepidocrocite-structure, $Na_{1-x}Ti_{2-y}\square_yO_4$
  - Prepared by ion-exchange from Cs-analog and post annealing
  - Na0.74Ti1.815O4: Up to 230 mAh/g at ~0.6 V vs. Na
  - Good cycle performance for 500oC annealed sample (~180 mAh/g)
  - Performance improvement by carbon coating

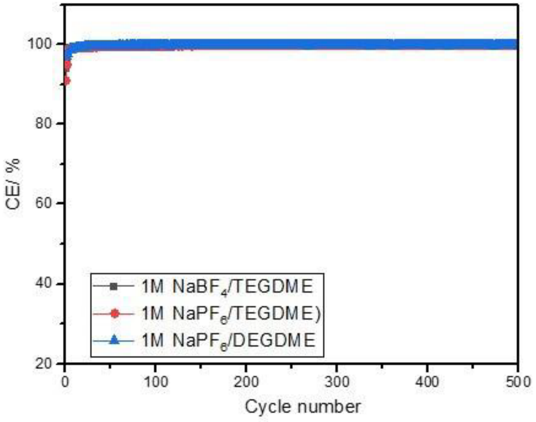


PNNL – Novel electrolytes

Electrolytes and interfaces for stable high-energy sodium-ion batteries

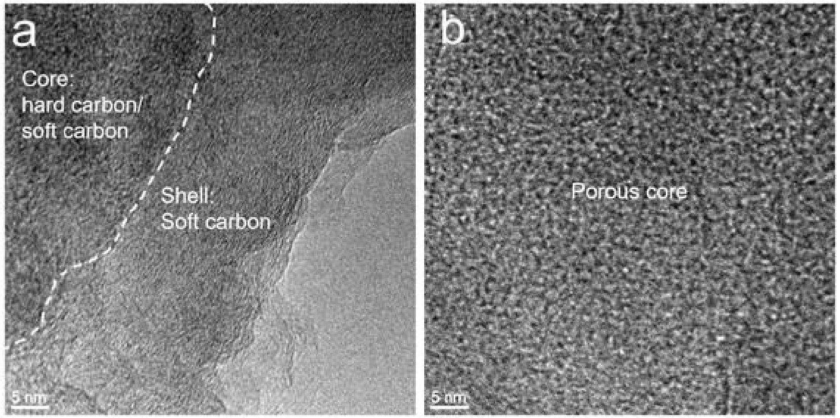
- PI: Phung M. Le (FY21-present) / Ji-Guang Zhang (FY19-FY21)
- Novel phosphate-based non-flammable electrolytes that are stable against HV cathodes and hard carbon anodes (FY19-FY22)
  - TEP-based LHCEs (e.g., NaFSI in TEP/TTE): decent cycle performance with HC and layered oxide cathodes
  - TFP-based LHCEs (e.g., NaFSI/DMC:TFP): Compatibility with polymer separator, Better high-voltage cycle stability
  - LHCE based on ether solvent (e.g., NaFSI/DME:TTE): Decent Na stripping/plating behavor
- From FY23, the development focus is re-directed to sustainable cathodes, specifically PB and NFM (in collaboration with ANL)

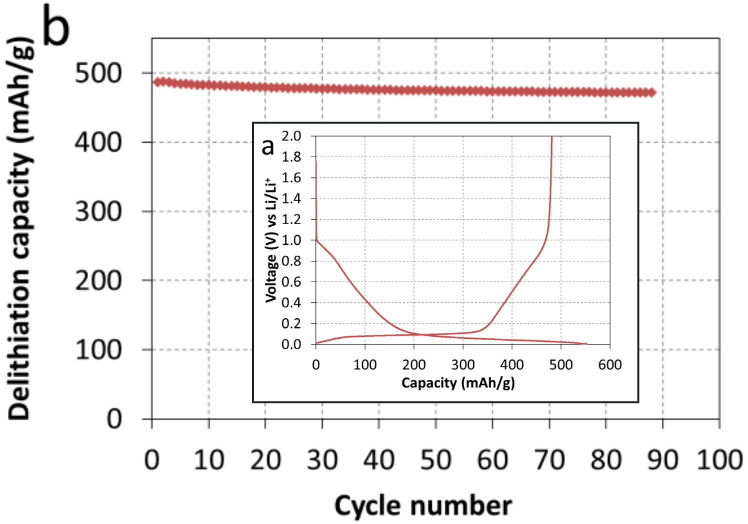


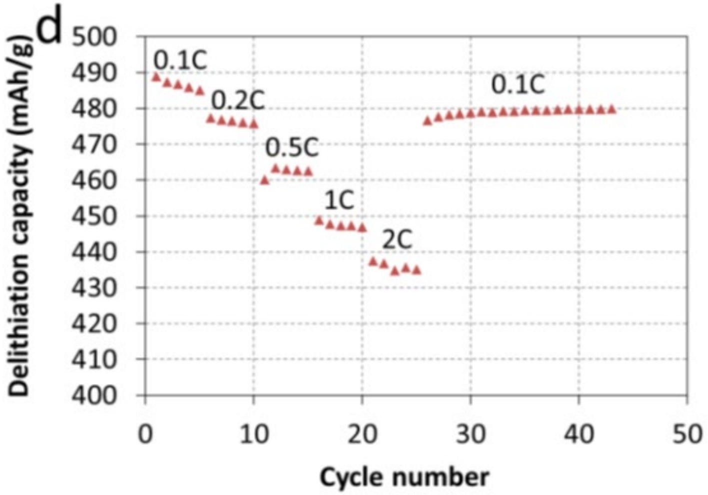


PNNL – Novel hard carbon anode (FY20-21)

- Developed high-capacity hard carbon anode with inner pore structure (> 450 mAh/g)
  - Closed pores (1-2 nm) inside the carbon structure with amorphous carbon shell (~20 nm)
  - Amorphous carbon shell prevent electrolyte diffusion (while allowing Na-ion diffusion) into inner pores minimizing side reaction
  - 1^{st} desodiation capacity ~490 mAh/g with 85% CE





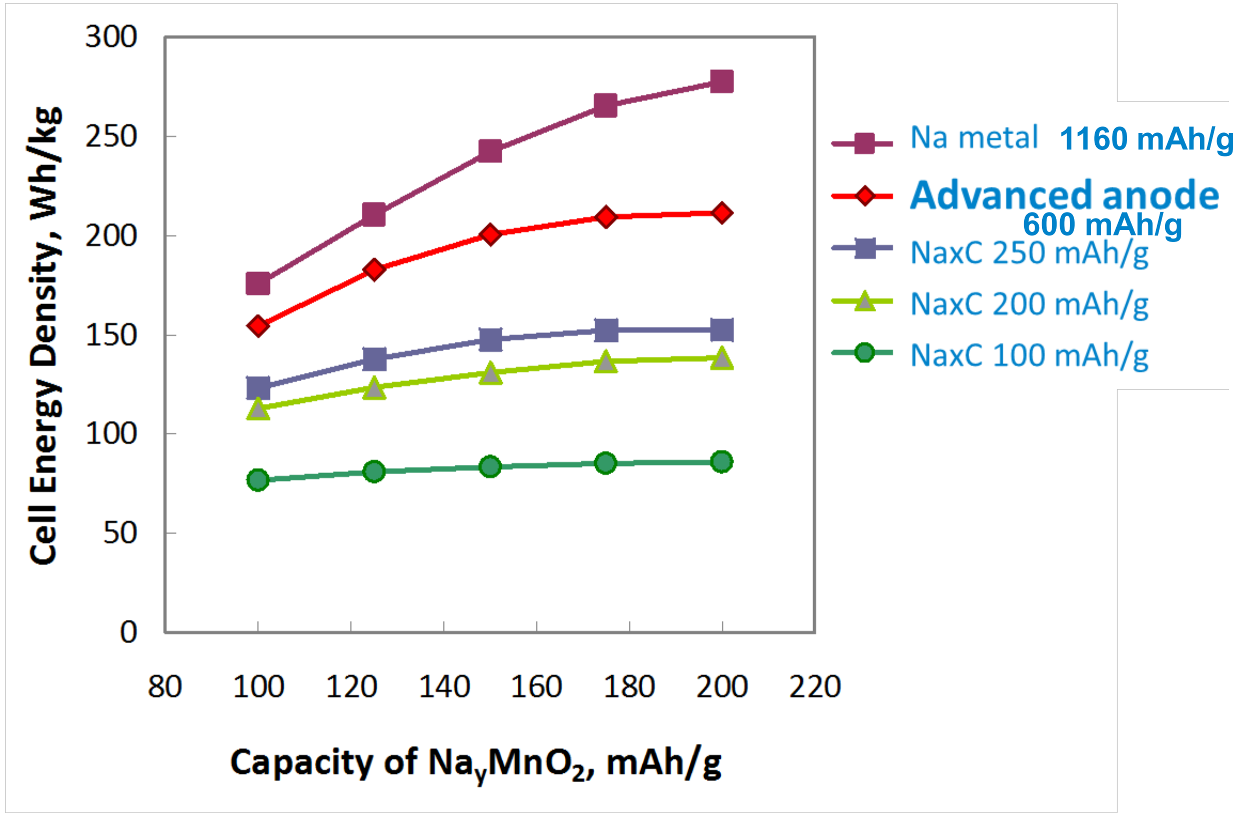


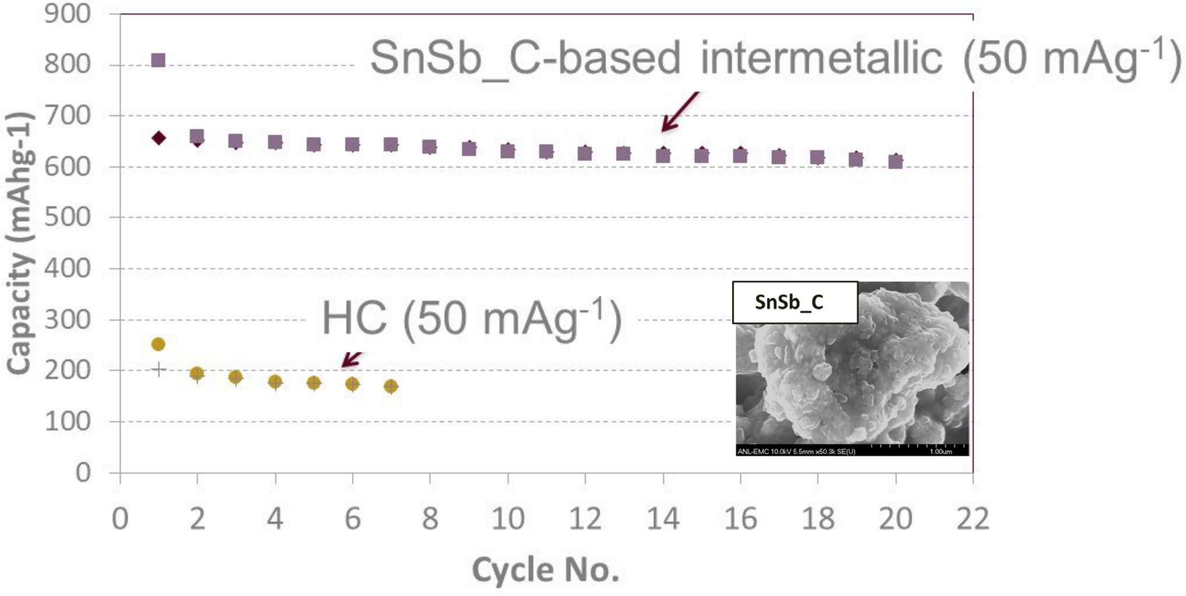
1M $NaPF_6$ in EC-DMC; 0.005 – 2.0 V @45 mA/g

J. Zhang et al. DOE BMR Report

Call for Advanced anodes

Energy Density range of Na-ion (3.0 V) – BatPaC# (ANL model) for transportation applications (Power/Energy ratio = 2)





*Energy density model : quite cell voltage dependent (4.0 V; 30-50% ↑)◊

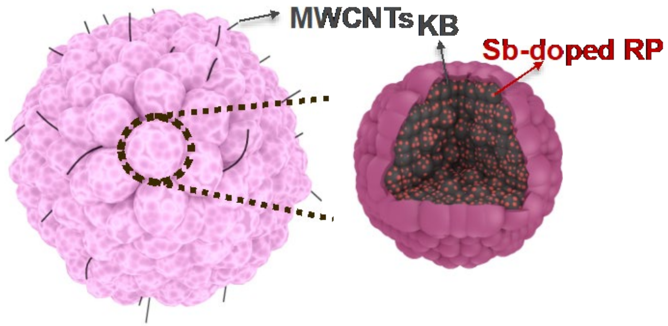
- http://www.cse.anl.gov/batpac/index.html

◊ Eroglu et al., *J. Power Sources*, **267**, 14 (2014)

Slater and Johnson et al. Adv. Funct. Mater. (2013)

ANL – PHOSPHORUS ANODES (AMINE) (FY19-23)

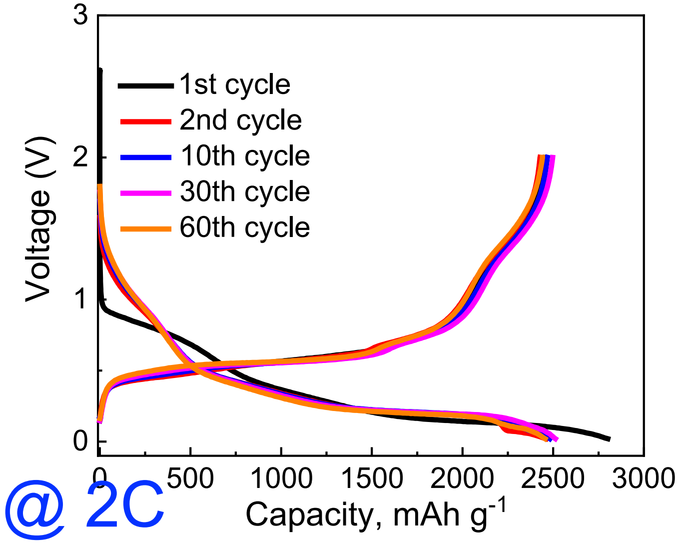
Light alloying anode



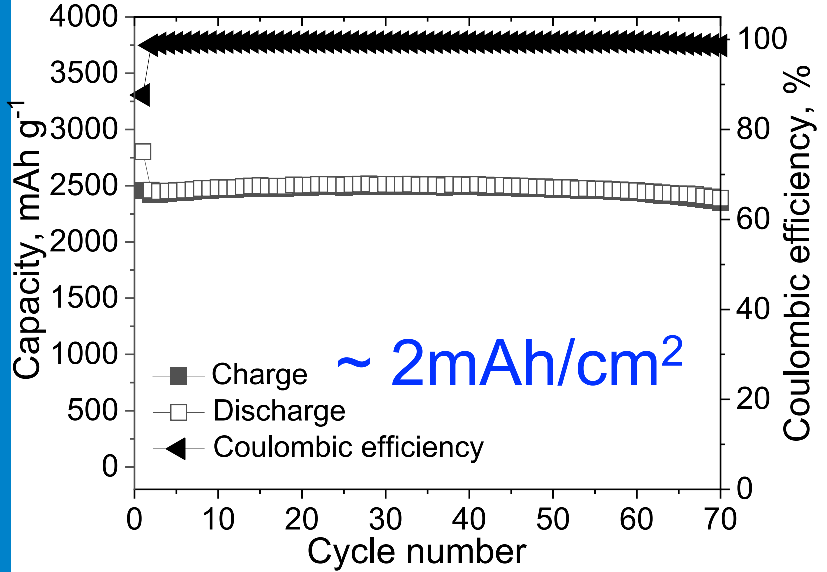
Sb_x-RP_{70-x}/KB-MWCNTs

Red P: low-cost
Sb-doping (Sb:RP=1:9, w/w):
Significantly increases the electronic conductivity

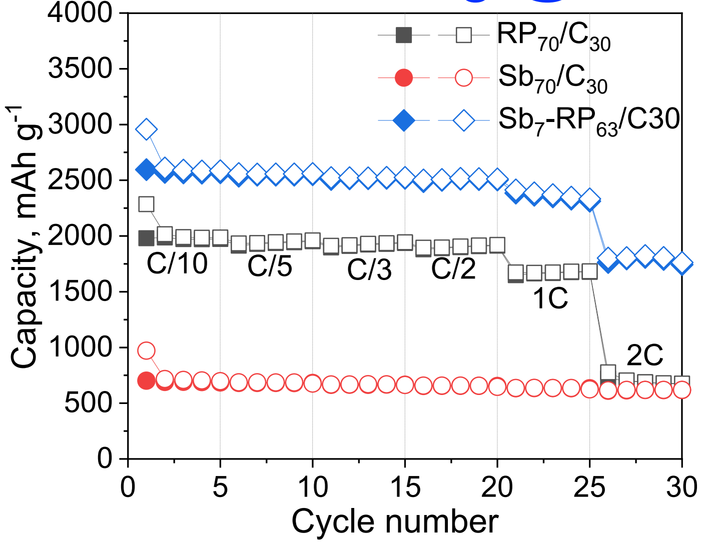
Plateau: 0.2-0.5V

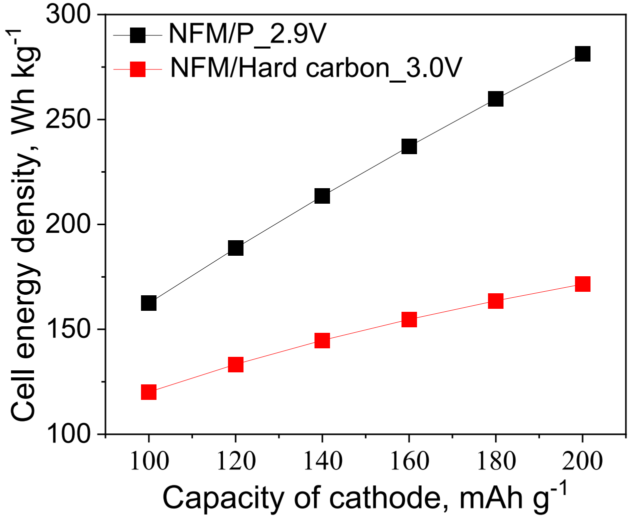


2500 mAh/g, ICE: 88%



~ 2000 mAh/g @ 2C

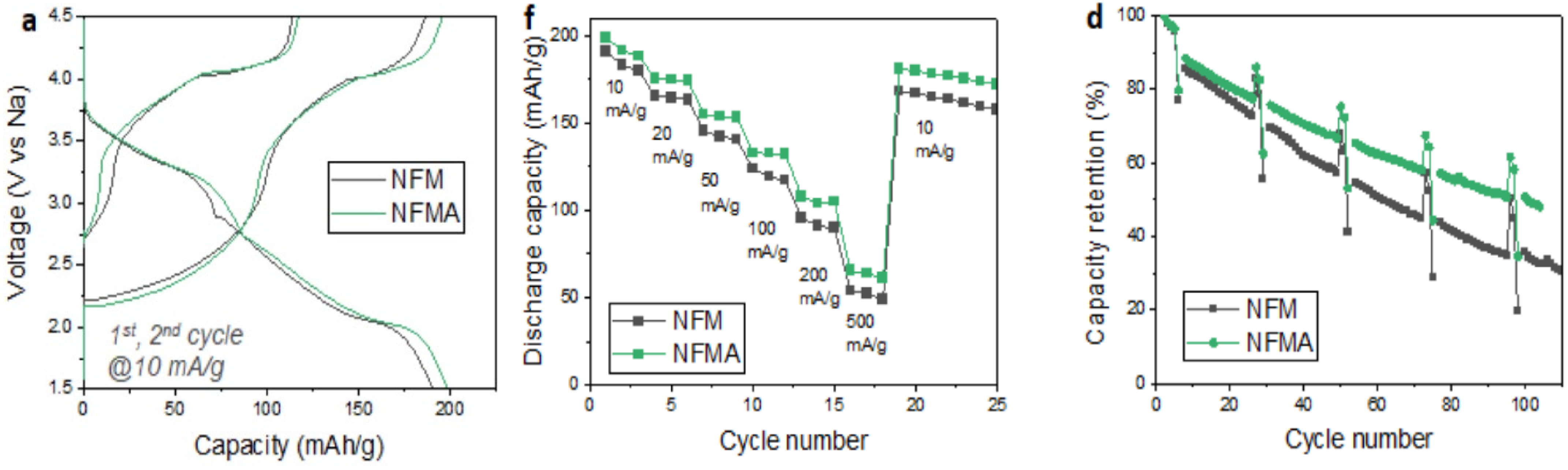




ANL – Sustainable Cathodes (Johnson) (FY19-23)

Focus on Fe & Mn and minimize Ni (no Co)

$Na_y(Fe_{1-x}Mn_x)O_2$



- Trying to enable Fe(III/IV) redox couple
- Needs improved electrolyte with additives
- Amenable to further metal doping
- Needs morphology control & better pCAM TM distribution
- FY'24 -> starting to work on full system with optimized electrolyte

CONCLUSIONS

- Much more work on sodium-ion is needed for transportation applications
  - Advanced anodes and higher voltages are needed to up the energy density
- Sodium-ion batteries show promise for alternative energy-storage to Li-ion
  - Push for low cost, good sustainability and non-constraining supply chains
- BMR projects are building towards a system with ~200 Wh/kg energy density
  - Graphite/LFP Li-ion cells are the storage benchmark to compete with
- Not shown here but reports on good low temperature performance and long-term cycling is very good

ACKNOWLEDGEMENTS

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THANKS FOR YOUR ATTENTION!