

DEVELOP HIGH-ENERGY SODIUM-ION BATTERY SYSTEMS

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Chemical Sciences and Engineering Division (CSE) Argonne National Laboratory Annual Merit Review DOE Vehicle Technologies Program Washington, DC June 10-13, 2019

Project ID # BAT430

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Overview

Timeline

- Start date: FY19
- End date: FY21
- Percent complete: 10%

Barriers

- Low energy density
- Cost
- Abuse tolerance limitations

Budget

- Total project funding: 100% DOE
- FY19 Funding: \$600K

Partners

- Co-PI: Chris Johnson, Khalil Amine
- Collaborators:
 - CSE, Argonne: Guiliang Xu, Eungje Lee, Jehee Park, Amine Daali, Jinhyup Han, Jiyeon Gim,
 - Faradion (UK): Jerry Barker



Relevance

- New battery chemistries are required in order to drive cost down for cells for transportation technologies with sufficient performance in volumetric energy density, and cycle life.
- The time-frame for introduction of new battery chemistry should be within a 5 year time-frame for commercialization.
- Chemistries targeted are earth-abundant, low-cost, safe and recyclable.
- Sodium-ion batteries (SIBs), while relatively new player in the field of batteries may well fulfill these requirements if deep understanding, good science and breakthroughs are made.



Figure CNRS (France; RS2E battery network) developed sodium-ion 18650 battery



Milestones

- This is a new project just initiated in January 2019.
- Objectives
 - The goal is a system that is at least 500 Wh/L volumetric energy density with over 500 cycles of operation in sodium-ion cell
- First and second year milestone
 - Develop an anode that is at least 600 mAh/g capacity overall and operating at <0.55 V vs sodium metal
- Second and third year milestone
 - Design, synthesize and develop a cathode that possesses at least 200 mAh/g capacity and >3 V operation
 - Complete full cell fabrication and echem metric testing



Approach

- Anode development
 - Create a phosphorous/metalloid/carbon composite with excellent safe performance at low cost
- Cathode development
 - Synthesize and design an intergrowth Fe-Mn containing layered sodium transition metal oxide cathode. Intergrowth will be an optimized P2/O1/O3 type structure that provide high capacity (>200 mAh/g) and high rate
 - Develop a full concentration gradient Fe/Mn-containing layered sodium oxide cathode
 - Use a stabilizing coating for the cathode interface
- Diagnostics
 - Make use of operando synthesis methods to hone in on the best conditions to make cathodes. i.e. temperature-dependent XRD used at APS
 - Study the safety of the materials using DSC, and evaluate 0 V battery storage (for safety, storing/transportation)



Argonne <u>BatPaC Calculations</u> for SIB battery pack for EVs

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oard 12 Font 12 Alignment	183 Total mass of pack extensions for air-cooled packs, kg 184 Battery jacket and hardware mass, kg	0.00	0.00	0.00	0.00	0.00	0.00	0.00 73.2											
	185 Pack integration unit (BMS & disconnects, ave. density = 1.0), kg	4.0	4.0	4.0	4.0	4.0	4.0	4.0											
▼ : × ✓ f _x Cost Breakdown Analysis	186 Mass of battery pack and integration unit, kg 187 Battery system volume (all packs), L	667.9 309.4	667.9 309.4	667.9 309.4	667.9 309.4	632.9 273.9	667.9 309.4	682.1 315.3											
B C D E F G H	18/ Battery system volume (all packs), L 188 Battery system mass (all packs), kg	667.85	309.4	309.4	309.4	632.92	667.85	682.08											
4% 5%	189 Battery Cooling System																		
Materia	190 Heat generation rate for battery system, W 191 Cooling System	392	392 Datia 4	392 Defin 4	392 Datia 4	422	392 Refrig 4	376					P/E (10-s), W/Wh						
8%	192 Mass and Volume of Cooling System Exterior to Battery Packs	Refrig 4	Refrig 4	Refrig 4	Refrig 4	Refrig 4	Kettig 4	Refrig 4				NCA-G	32						
- Purcha	193 Mass, kg	7.0	7.0	7.0	7.0	7.0	7.0	7.0				NMC622-G	36						
	194 Volume, L 195 Vehicle Electric Parameters	2.8	2.8	2.8	2.8	2.8	2.8	2.8				LFP-G LMO-G	28						
3%	196 Energy requirement of whicle on LIDDS cycle (default = 250) Wh/mil	e 250.0	250.0	250.0	250.0	250.0	250.0	250.0				250.0	250.0	250.0	250.0	250.0	250.0	250.0	
Variab	197 Energy requirement of battery pack, Wh/mile	250.0	250.0	250.0	250.0	250.0	250.0	250.0				250.0	250.0	250.0	250.0	250.0	250.0	250.0	
	198 Available battery energy, % of total	85	85	85	85	85	85	85				85	85	85	85	85	85	85	
Genera	199 Vehicle electric range, miles	340.00	340.00	340.00	340.00	340.00	340.00	340.00				0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	200 Pack Capacity Calculation 201 Select capacity, battery energy, or vehicle range, but only one.											0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	202 Pack capacity (Ah)																		
28%	203 Pack energy (kWh) 204 Vehicle range (miles)	100.0	100.0	100.0	100.0	100.0	100.0	100.0				5.56	5.56	5.56	5.56	5.56	5.56	5.56	
		89.3	89.3	89.3	89.3	178.6	89.3	148.8											
Profit	206 Capacity at C/3, Ah	90.14887		90.14887	90.14887	180.43114		150.19038											
- 14/	207 Capacity (holding)	90.14887	90.14887	90.14887	90.14887	180.43114		150.19038											
warra	208 Convergence constant 209 Positive electrode thickness	44.6	44.6 7 120.125287	44.6	44.6	89.3	44.6	74.4											
	210 Positive electrode thickness (holding)	120.12528		120.12528			120.125207	120.125287											
	211 Convergence constant	0.5	0.5	0.5	0.5	0.5	0.5	0.5											
Materials and Purchased Items Co	212 Addition to cell thickness to adjust for whole number of electrodes	-0.169136 -0.169136		-0.169136 -0.169136				-0.169147 -0.169147											
	213 Addition to cell thickness (holding) 214 Convergence constant	0.1	-0.169136 0.1	0.169136	0.169136	0.1	-0.169136	-0.169147											
Battery 1	215 Restart (0/1		1	1	1	1	1	1											
Positive Active Negative Carbon and Material Negative Carbon and	216																		
Material Active Binders 8% Material 5%	217 Battery System Values 218 Power, kW		200.0	200.0	200.0	200.0	200.0	200.0											
Battery 0% Positive	219 Energy, kWi	h 100.00	100.00	100.00	100.00	100.00	100.00	100.00											
Jacket Current	220 Mass, kg	g 667.9	667.9 309.4	667.9 309.4	667.9 309.4	632.9 273.9	667.9 309.4	682.1 315.3											
12% Collector 3%	221 Volume, I 222 Wh/kg		309.4	309.4	309.4	158	309.4	315.3											
	223 Wh/t	L 323	323	323	323	365	323	317											
Module Negative Current	224 S/kWr , 225 Estimated Total Battery Cost to OEM, US3		97 9,709	97 9,709	97 9,709	82 8,154	97 9,709	98 9,824		_									
Collector	226 Estimated Cell Cost to OEM, US\$/Cel	II 15.9	15.9	15.9	15.9	28.9	15.9	13.6											
24% 11%	1 227 Estimated Cell Cost to OEM, US\$/kWi		63.5 549.0	63.5 549.0	63.5 549.0	57.9 570.7	63.5 549.0	65.1 542.3											
Separators	228 Cell Energy Density, Wh/l 229 Cell Specific Energy, Wh/ke	a 181.2	181.2	181.2	181.2	184.2	181.2	542.3											
18%	About BatPaC Chem Battery Design EV Ch	harging	Summary of R	esults U	SABC Data	Thermal	Cost Input	Manufactu	ring Cost Calculations	Prices of C	ells and Mod	ules Cost	Breakdown	Recycle	Plant Sche	matic Ce	ll De (+) : 4	
Cell Hardware Electrolyte	Ready Calculate					_	and a good of the												1
Cell Hardware	Cell Hardware																	_	-
	Module Hardware																		
	Battery Jacket																		
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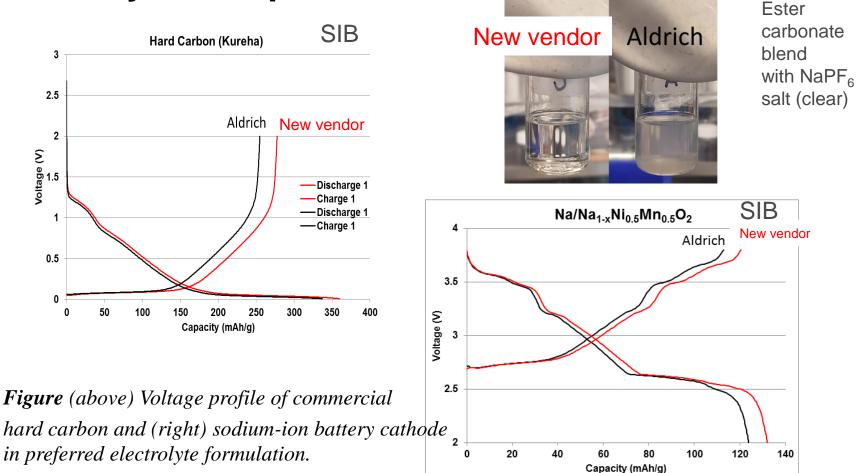
BatPaC modeling shows that a volumetric energy density for SIB at 549 Wh/L is possible. Cost is projected at \$63.5/kWh.

S. Ahmed, 2019 (Argonne)



Technical Accomplishments

Identification of suitable commercial electrolyte completed



New commercial battery grade $NaPF_6$ is adequate for use for SIB work/research in this project

Han, Park, Lee, 2019 (Argonne)



Development of recyclable Pb and Pboxide carbon composites as energy dense anodes - synthesis

- Lead oxide : carbon = 7 : 3 weight ratio
- Lead oxide sources: PbO and Pb3O4
- Carbon sources: super P and C45 (Timcal) carbon black
- Added, Stainless jar and sealed in glove box.
- The sealed jar was shaken in SPEX 8000M MILL GRINDER for 6h



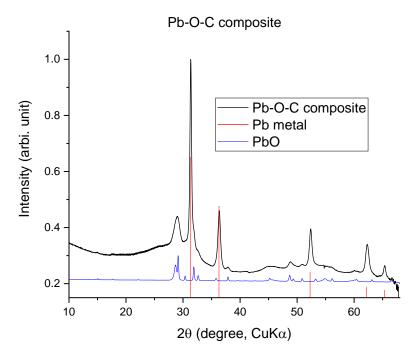
Method	Compound	Electrode laminate
Spexmill	Pb-O-C composite #1 (from PbO)	Active : Carbon : PVDF = 8 : 1 : 1
Spexmill	Pb-O-C composite #2 (from Pb ₃ O ₄)	Active : Carbon : PVDF = 8 : 1 : 1
	Commercial PbO (SIGMA)	Active : Carbon : PVDF = 7 : 2 : 1
	Commercial Pb ₃ O ₄ (SIGMA)	Active : Carbon : PVDF = 7 : 2 : 1
	Super-P	Carbon : PVDF = 9 : 1

A Pb based anode system in a SIB battery system can be recycled by the leadacid battery industry thus providing a potential revenue stream to recycling companies.

J. Han and E. Lee, 2019 (Argonne)



Development of recyclable Pb and Pboxide carbon composites as energy dense anodes – XRD results



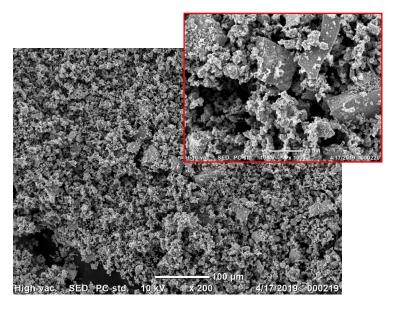


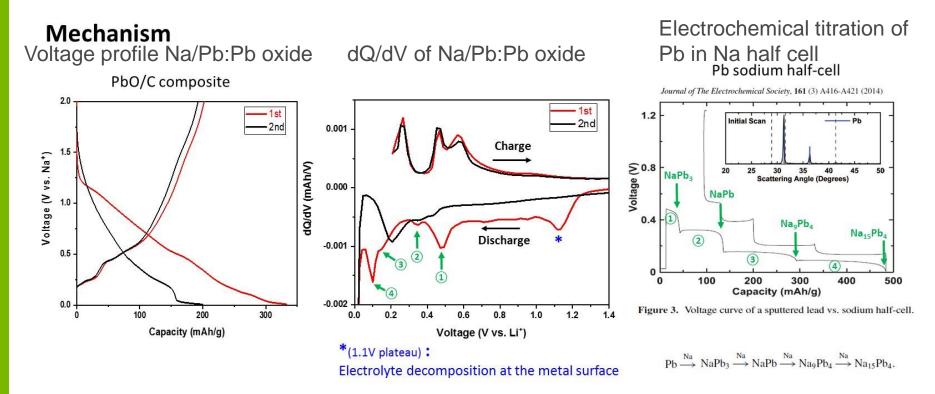
Figure XRD pattern (left) and SEM image (right) of the Pb-O-C composite sample made by HEBM. The mechanochemical carboreduction of lead oxide in presence of carbon resulted in Pb metal in the matrix of PbO-C composite.

Ball milling lead oxides (PbO or Pb_3O_4) with carbon makes Pb metal in a sea of oxide matrix together with carbon composite

J. Han and E. Lee, 2019 (Argonne)

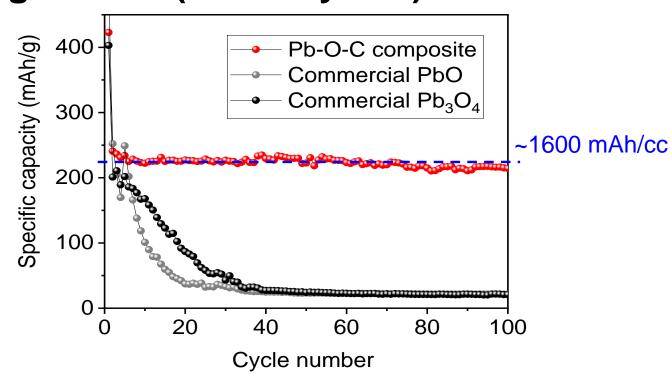


Development of recyclable Pb and Pboxide carbon composites as energy dense anodes – battery (coin cell) cycling results (first 2 cycles)



Voltage profile follows the expected electrochemical pathway in the literature

Technical Accomplishments Development of recyclable Pb and Pboxide carbon composites as energy dense anodes – battery (coin cell) cycling results (first 2 cycles)



Cycle stability is good. Since Pb density is 11.36 g/cc and Pb_3O_4 is 9.53 g/cc; we take the overall density of the material as about 8 g/cc (carbon is in it). Thus the volumetric energy density is 1600 mAh/cc (c.f., graphite (LIB) is ~600 mAh/cc, and Si (LIB) ~2200 mAh/cc). 1.1

J. Han and E. Lee, 2019 (Argonne)



Black Phosphorus provides good anode performance – >1500 mAh/g (100 cycles)

Technical Accomplishments

Data from Co-PI, K. Amine

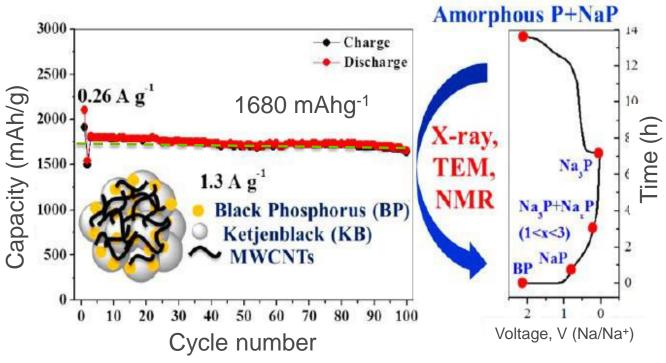


Figure Structure scheme, cycle performance and sodiation/de-sodiation mechanism for the black phosphorus/Ketjenblack composite.

High capacity and good cycle life of black phosphorus/Ketjenblack composite was achieved because of high sodiation/de-sodiation reversibility.

Xu, and Amine (Argonne); published in Nano Letters 2016

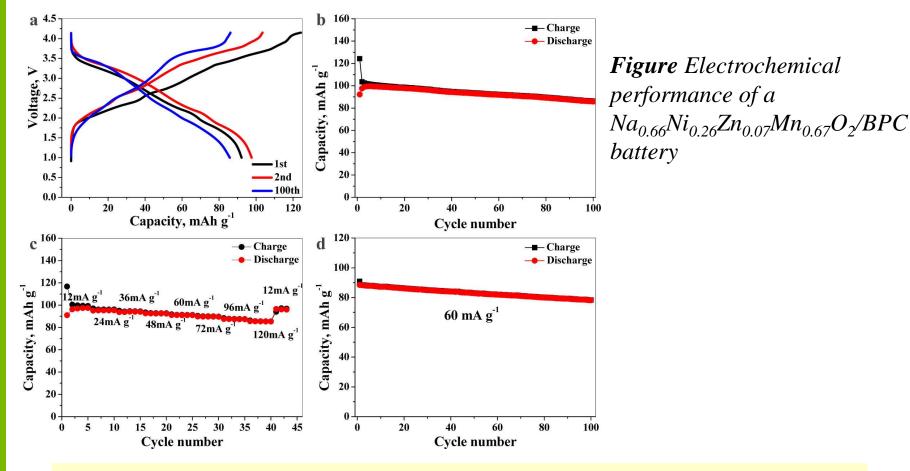


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High performance when served as anode in full cell

Technical Accomplishments

Data from Co-PI, K. Amine



Good stability of black phosphorus/Ketjenblack composite in full cell was successfully demonstrated.

Xu, and Amine (Argonne); published in Nano Letters 2016

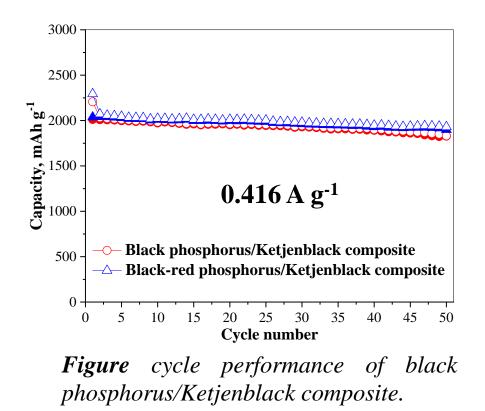


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Blend of black and red phosphorus to lower cost and maintain high performance

Technical Accomplishments

Data from Co-PI, K. Amine



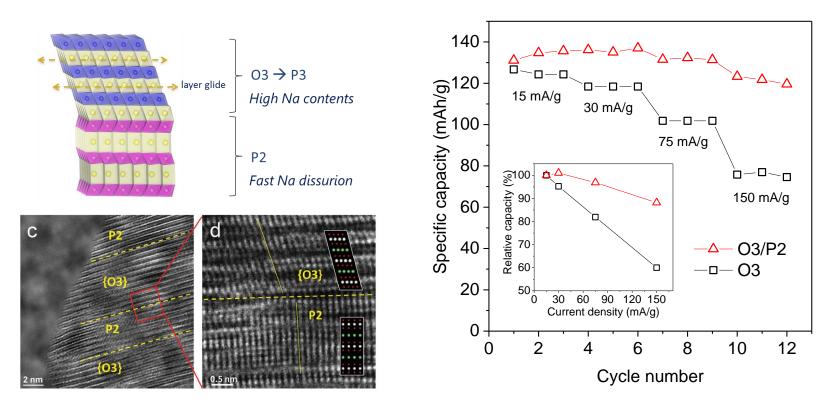
We are compositing red Phosphorus (inexpensive polymorph @ \$40/kg) with doping of Black P and carbon black as conductive diluent

Xu, and Amine (Argonne), U.S. patent application US20170214035A1;



Technical Accomplishments

Cathode work: Intergrowth layered structures provide high-capacity and high-rate performances



Synergistic performance enhancement mechanism via O3/P2 layer intergrowth structurers was first reported by Argonne team.

Lee, Johnson, et al. Adv. Energy Mater. 2014, 4, 1400458

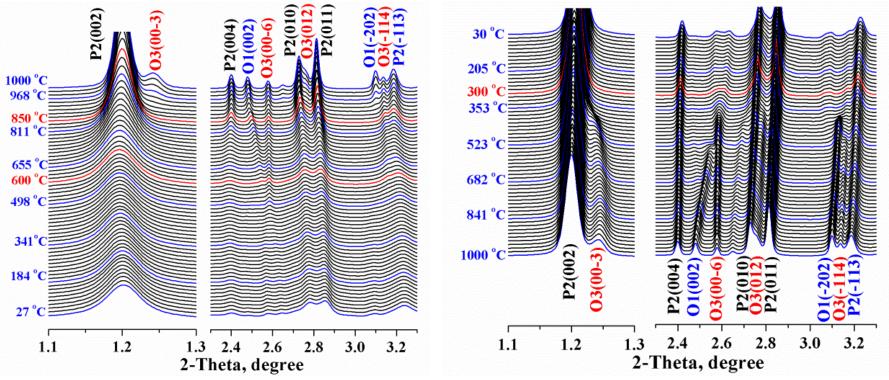


Cathode work: Understand the sintering process by operando Synchrotron HEXRD

Technical Accomplishments

Data from Co-PI, K. Amine

Real-time observation of structure evolution



Triple-phase formed at high temperatures; Triple-phase disappeared during the cooling process;

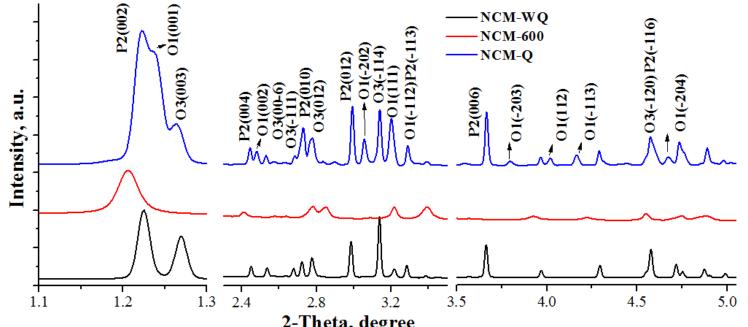
Xu, Chen, Amine et al. Energy Environ. Sci. 2017, 10, 1677-1693



Controlled the crystal structure of the materials through controlling the sintering condition

Technical Accomplishments

Data from Co-PI, K. Amine



2-Theta, degree

	Structure	Temperature	Time	Heat rate	Cool rate	Quench
NCM-Q	P2+O3+O1	850 °C	12 h	3 °C/min	1 °C/min	Yes
NCM-WQ	P2+O3	850 °C	12 h	3 °C/min	1 °C/min	No
NCM-600	P2+P3	600 °C	10 h	3 °C/min	1 °C/min	No

Xu, Chen, Amine et al. *Energy Environ.* ¹⁷Sci. 2017, 10, 1677-1693



Triple-phase intergrowth structure significantly increase the reversible Da capacity, cycle stability and rate capability

200 160 140 160 **—NCM-600** P2+03+01 ່ໝ 120 Capacity, mAh g⁻¹ Capacity, mAh 120 100 P2+O3 P2+O3+O1 80 P2+O3 80 60 P2+P3 40 P2+P3 **40** 20 0 20 25 35 40 45 50 5 30 0 2 3 4 1 Cycle number C-rate, C

> Cycle performance: P2+O3+O1>P2+O3>P2+P3 Rate capability: P2+O3+O1>P2+O3>P2+P3

Xu, Chen, Amine et al. *Energy Environ.* ¹⁸*Sci.* 2017, 10, 1677-1693



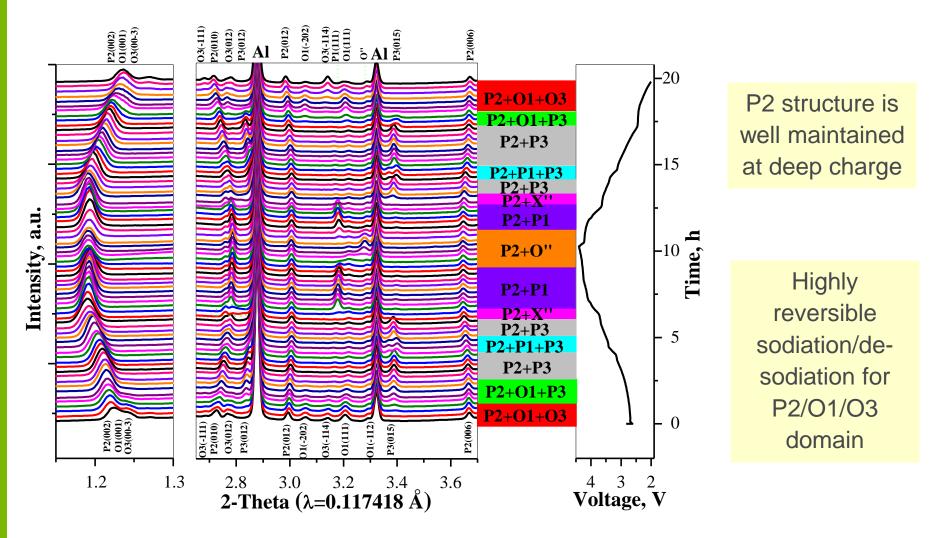
Technical Accomplishments

Data from Co-PI, K. Amine

Operando HEXRD of P2/O1/O3 during the 1st cycle showing high sodiation/desodiation reversibility process

Technical Accomplishments

Data from Co-PI, K. Amine



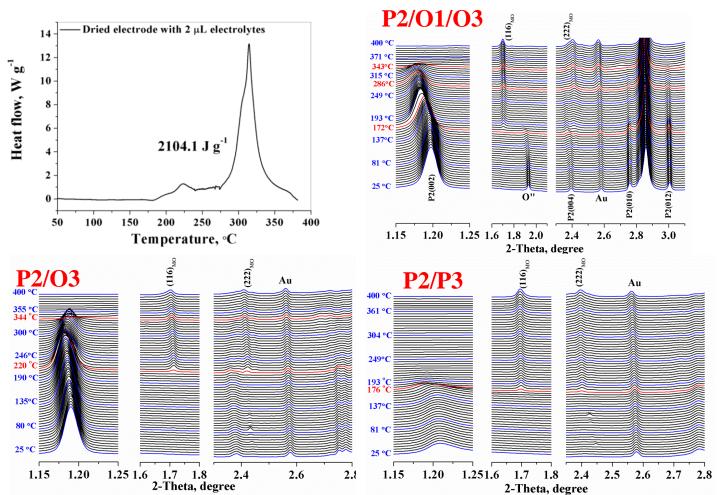
Xu, Chen, Amine et al. *Energy Environ.* ¹⁹*Sci.* 2017, 10, 1677-1693



Technical Accomplishments

Triple-phase intergrowth structure also improve the thermal stability

Data from Co-PI, K. Amine



Major heat come from generation of $(222)_{MO.}$ This temperature was lower from 286 °C (P2/O1/O3) to 220 °C (P2/O3) and 176 °C (P2/P3).

Xu, Chen, Amine et al. *Energy Environ.* ²⁰*Sci.* 2017, 10, 1677-1693



Summary

- BatPac calculation indicates sodium-ion battery can have a cost competitive advantage when the cell is designed with low-price, highperformance electrode couples.
- New Pb-based composite anodes provide high volumetric energy density and good cycle stability. The performance could be further improved by the morphology optimization and alloying strategies.
- Synchrotron X-ray diffraction was used to track the phase evolution during synthesis, charge/discharge and thermal runaway, providing good guidance for the design of better battery material
- Intergrowth layered structured cathode materials demonstrate both excellent electrochemical performance and high safety
- Phosphorus-based anode materials deliver highest reversible capacity and suitable working voltage, and a rational host design to accommodate the volume changes during cycling is the key to achieve long cycle stabi



Proposed Future Research

Year 1

- Optimization of carbon host to achieve high reversible capacity and long cycle life using red or blend (red/black) phosphorus anode materials
- Surface modification on the anode materials to stabilize the interface
- Make Na-Pb Zintl phases and check echem performance
 - A process to introduce more Na cations into SIB
- Start performance and optimization of the Red P/Pb-oxide/Pb carbon composite (PPbOC) composition for anode testing in SIB
 - Evaluate the stability of the PPbOC material
 - Rate, air stability, processing, etc.
 - Maximize the overall volumetric ED
 - Evaluate the reaction mechanism at play

Year 2

- Initiate cathode work
- Development of high tap density layered cathodes for SIBs
- Development of full concentration gradient layered cathodes for SIBs
- Surface modification using atomic layer deposition to protect layered cathodes from cracking, electrolytes penetration and oxygen loss during high-voltage charge



Acknowledgments & Collaborations

- Thanks to Tien Duong and David Howell for their support of this project
- Thanks to DOE EERE for funding



Response to Previous Year Reviewer Comments

New project initiated in FY '19



Remaining Challenges and Barriers

Technical

- Improve the first cycle ICL for Pb-based anode composite
- Understanding the SEI and the role of FEC as additive in the Red/Black P and Pb-based composites is critical to long cycle life (goal is 500 cycles)
- The synthesis of Fe-Mn sodium transition metal layered oxides whereby the Fe⁴⁺ cation is stabilized in the structure
- Formulate new electrolyte salts and additives. Involve an electrolyte expert either from industry or Argonne
- Building and optimizing full coin cells
- Scale-up of active materials to allow for building of pouch cells in the second year

Non-Technical

- Market, educate, and stimulate the battery industry to SIBs and their potential for:
 - Low cost, stability, safety and performance
 - Back-up technology to LIB; existing lines can be used

