DEVELOP HIGH-ENERGY SODIUM-ION BATTERY SYSTEMS

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DOE Vehicle Technologies Program
Washington, DC
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Project ID # BAT430

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)

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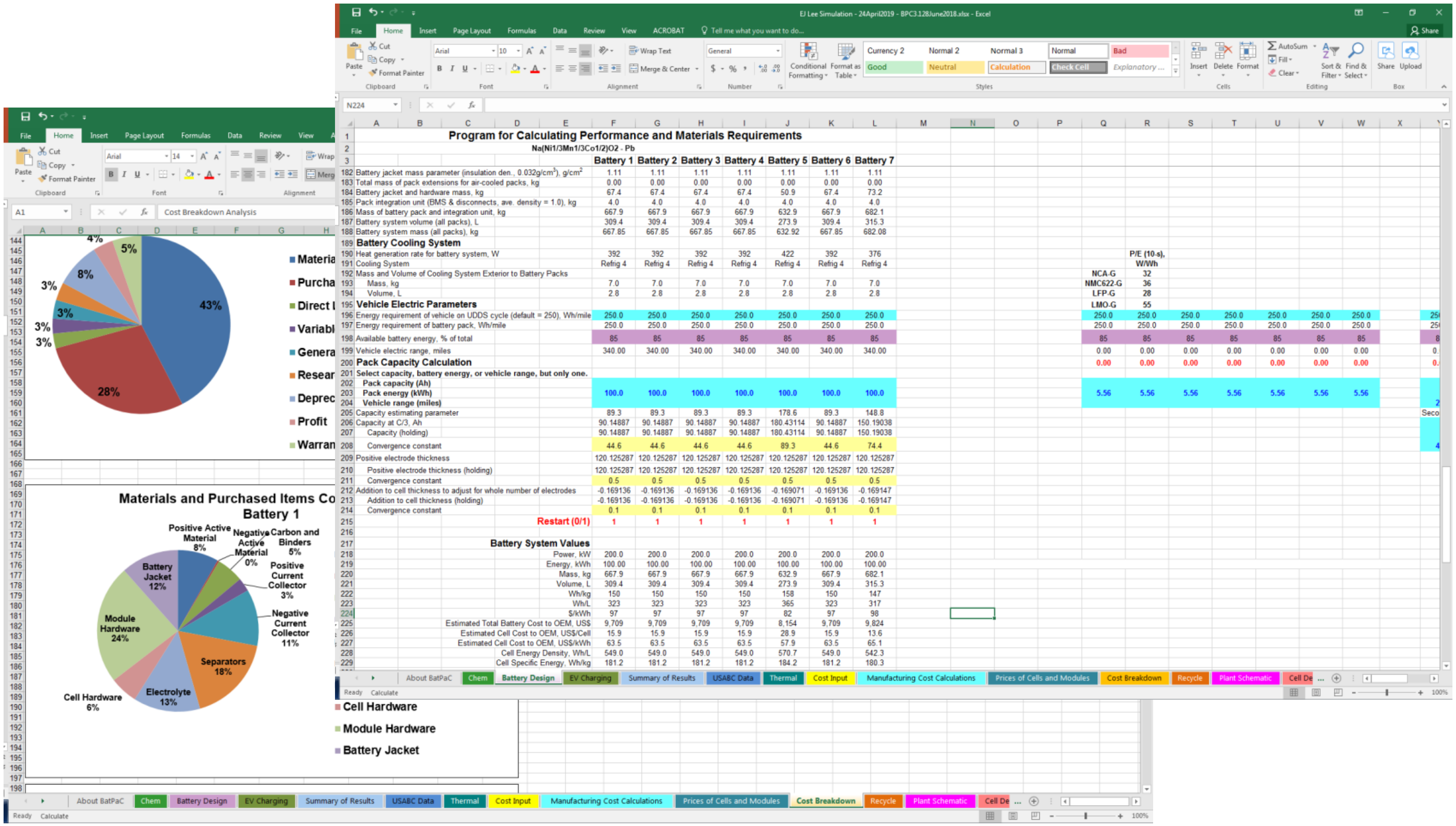
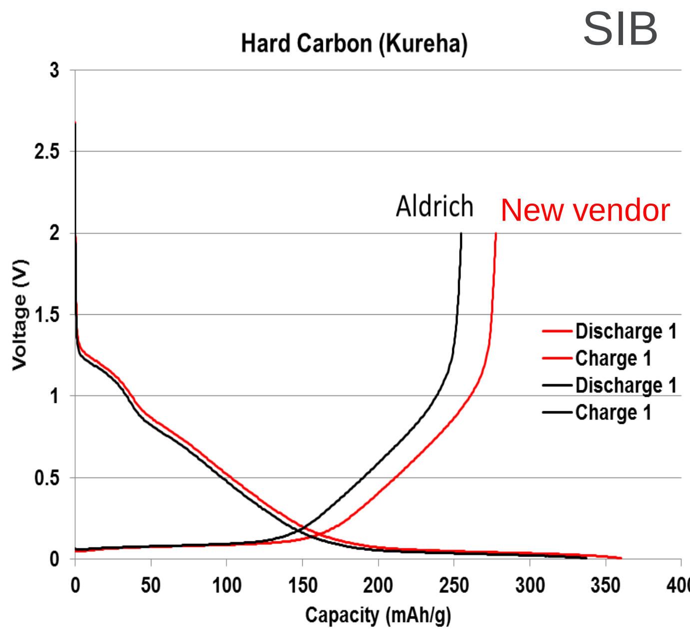
Argonne BatPaC Calculations for SIB battery pack for EVs

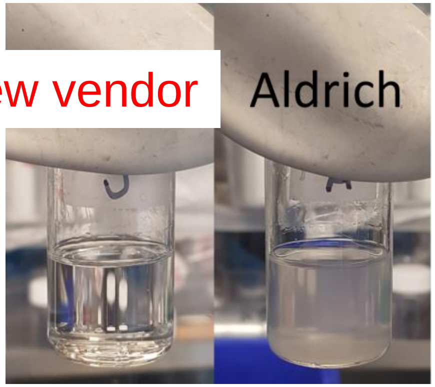


BatPaC modeling shows that a volumetric energy density for SIB at 549 Wh/L is possible. Cost is projected at $63.5/kWh.

S. Ahmed, 2019 (Argonne)

Identification of suitable commercial electrolyte completed





Ester carbonate blend with $NaPF_6$ salt (clear)

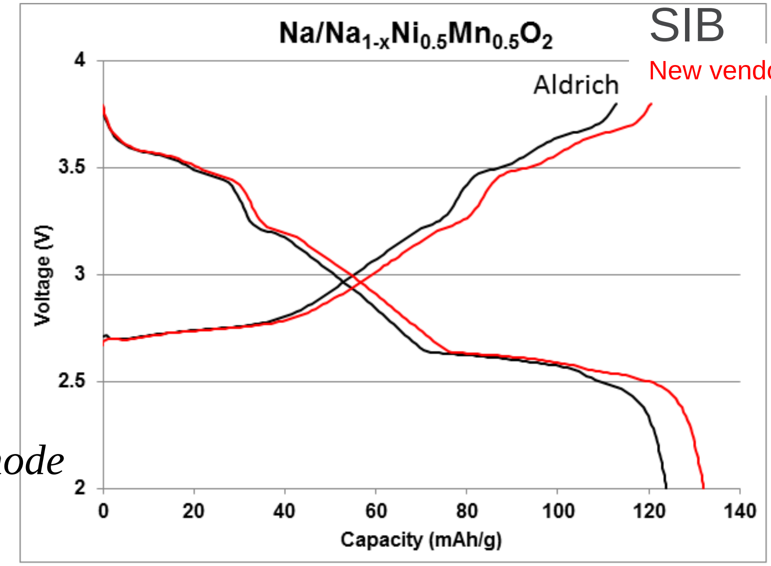


Figure *(above) Voltage profile of commercial hard carbon and (right) sodium-ion battery cathode in preferred electrolyte formulation.*

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

Han, Park, Lee, 2019 (Argonne)

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

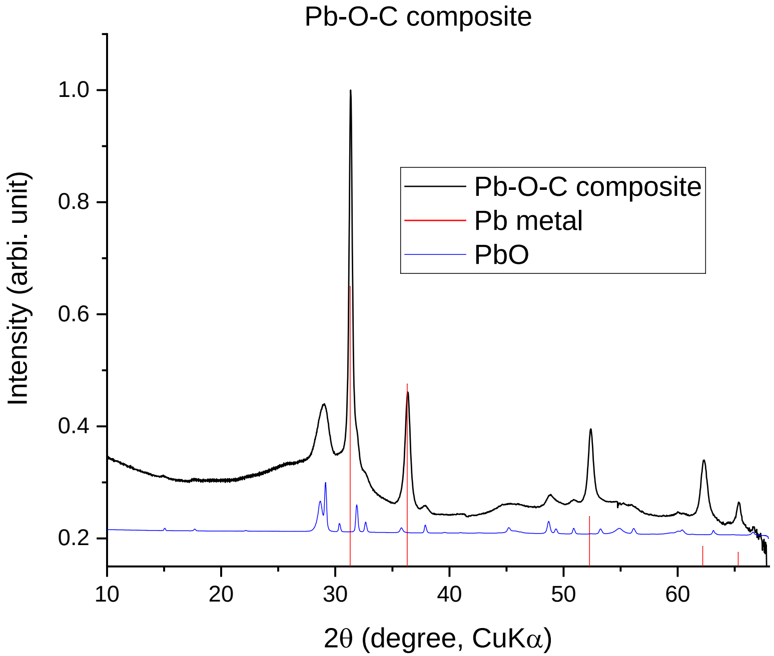
- Lead oxide : carbon = 7 : 3 weight ratio
- Lead oxide sources: PbO and Pb3O4
- Carbon sources: super P and C45 (Timcal) carbon black
- Added, Stainless jar and sealed in glove box.
- The sealed jar was shaken in SPEX 8000M MILL GRINDER for 6h

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_3O_4)	Active : Carbon : PVDF = 8 : 1 : 1
	Commercial PbO (SIGMA)	Active : Carbon : PVDF = 7 : 2 : 1
	Commercial Pb_3O_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 lead-acid battery industry thus providing a potential revenue stream to recycling companies.

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

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



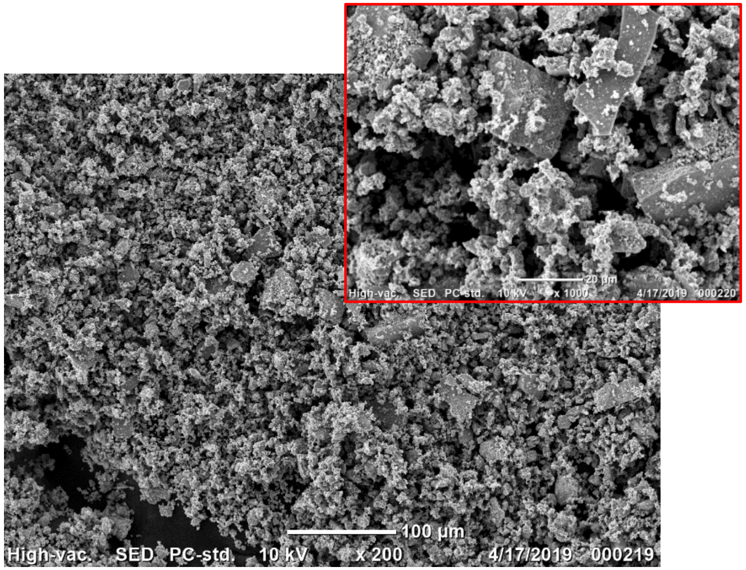


Figure *XRD pattern (left) and SEM image (right) of the Pb-O-C composite sample made by HEBM. The mechanochemical carboreduction of lead oxide in presence of carbon resulted in Pb metal in the matrix of PbO-C composite.*

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

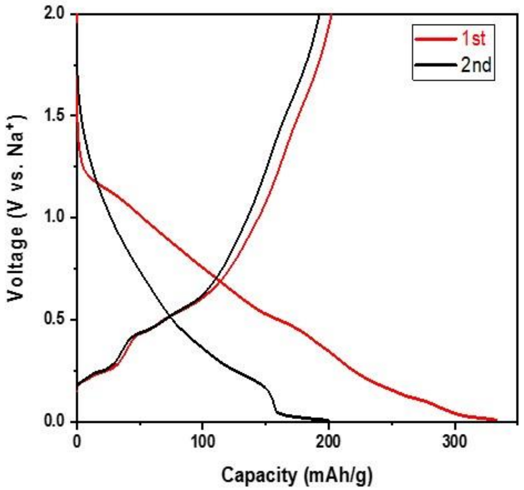
J. Han and E. Lee, 2019 (Argonne)

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

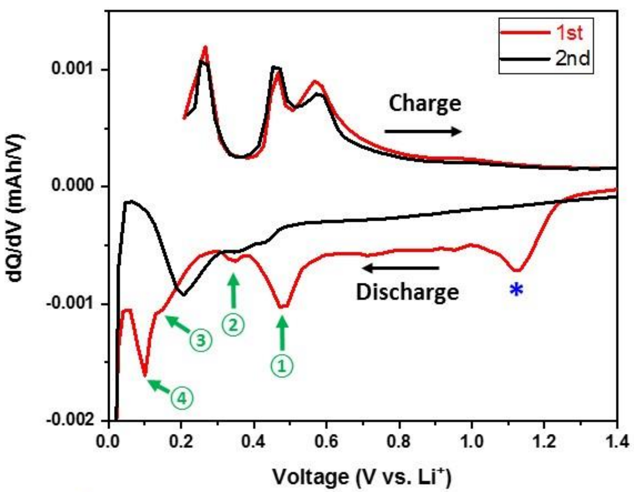
Mechanism

Voltage profile Na/Pb:Pb oxide

PbO/C composite



dQ/dV of Na/Pb:Pb oxide



*(1.1V plateau) :
Electrolyte decomposition at the metal surface

Electrochemical titration of Pb in Na half cell

Pb sodium half-cell

Journal of The Electrochemical Society, **161** (3) A416-A421 (2014)

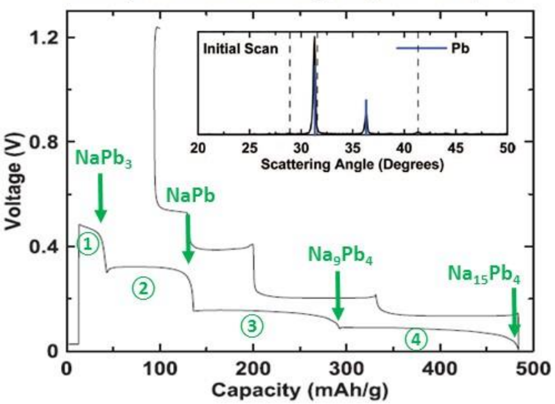


Figure 3. Voltage curve of a sputtered lead vs. sodium half-cell.

$$Pb \xrightarrow{Na} NaPb_3 \xrightarrow{Na} NaPb \xrightarrow{Na} Na_9Pb_4 \xrightarrow{Na} Na_{15}Pb_4.$$

Voltage profile follows the expected electrochemical pathway in the literature

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

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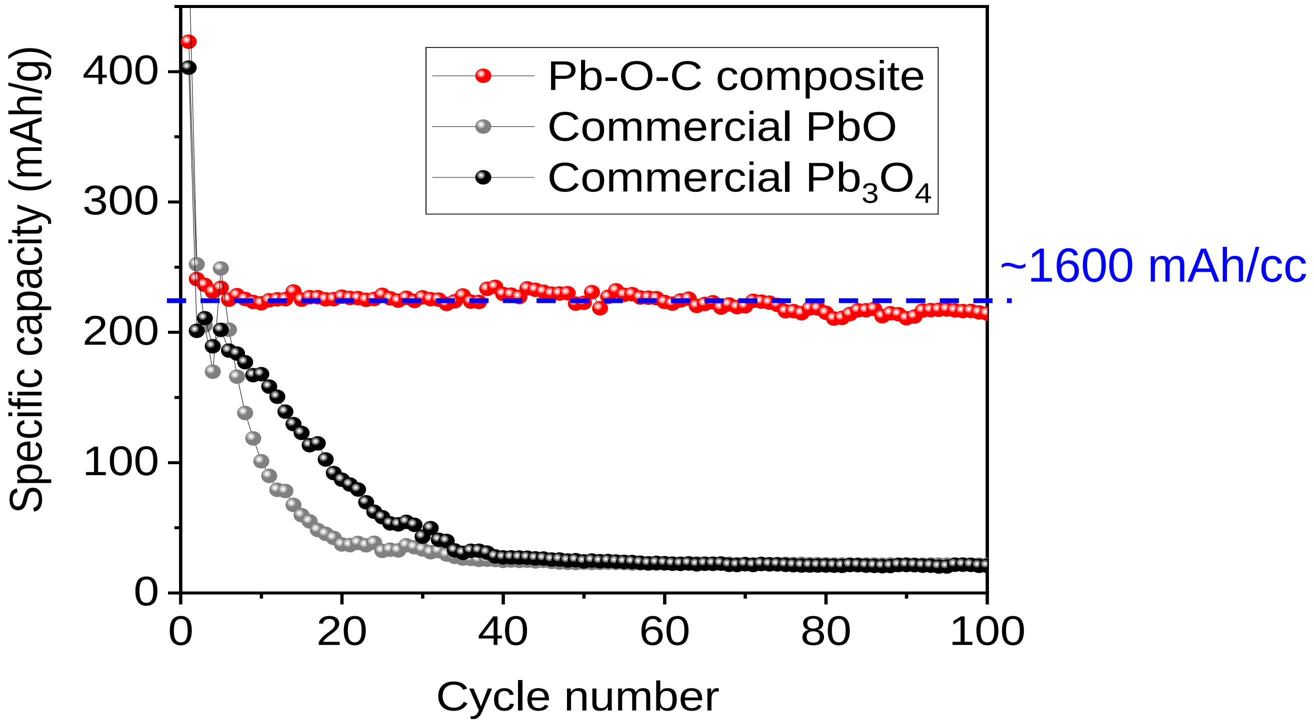
Development of recyclable Pb and Pb-oxide carbon composites as energy dense anodes – battery (coin cell) cycling results (first 2 cycles)



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).

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

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

Data from Co-PI, K. Amine

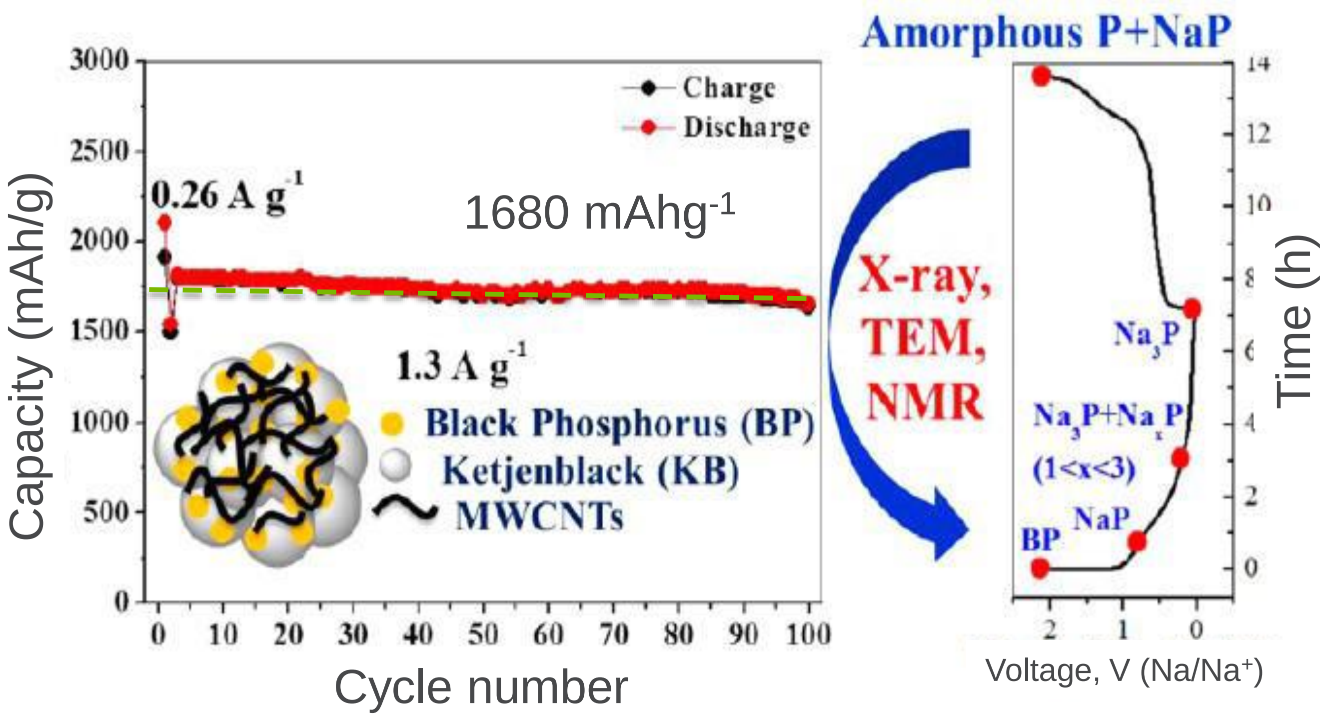


Figure *Structure scheme, cycle performance and sodiation/de-sodiation mechanism for the black phosphorus/Ketjenblack composite.*

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

High performance when served as anode in full cell

Data from Co-PI, K. Amine

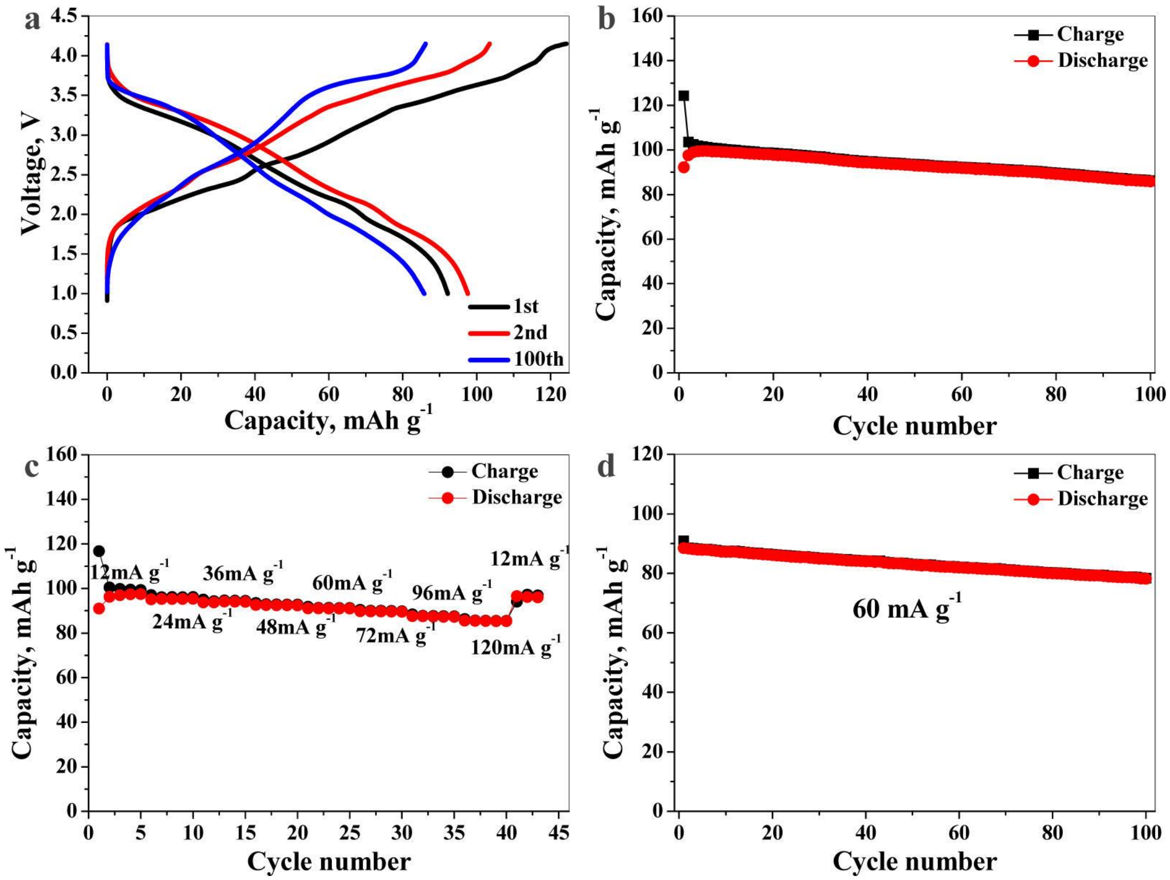


Figure *Electrochemical performance of a $Na_{0.66}Ni_{0.26}Zn_{0.07}Mn_{0.67}O_2$/BPC battery*

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

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

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

Data from Co-PI, K. Amine

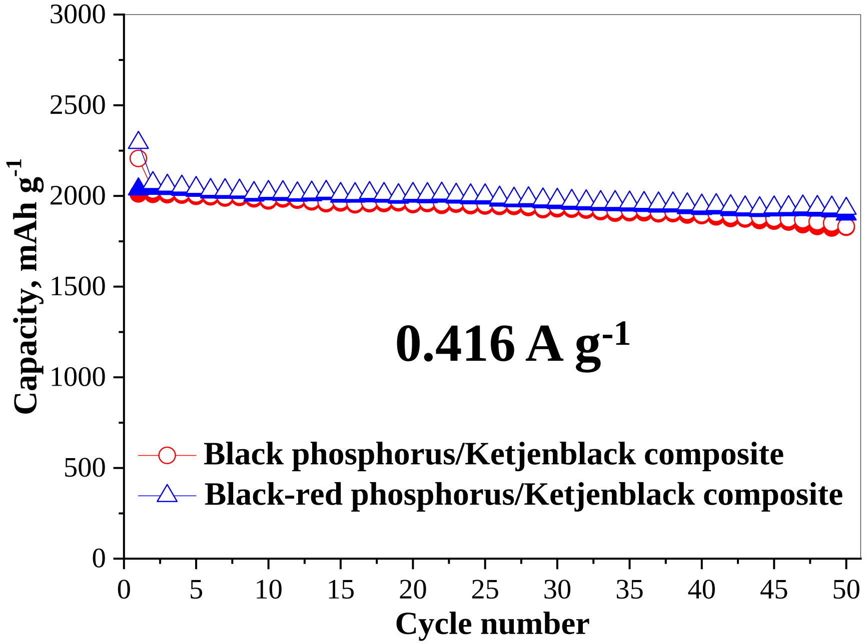
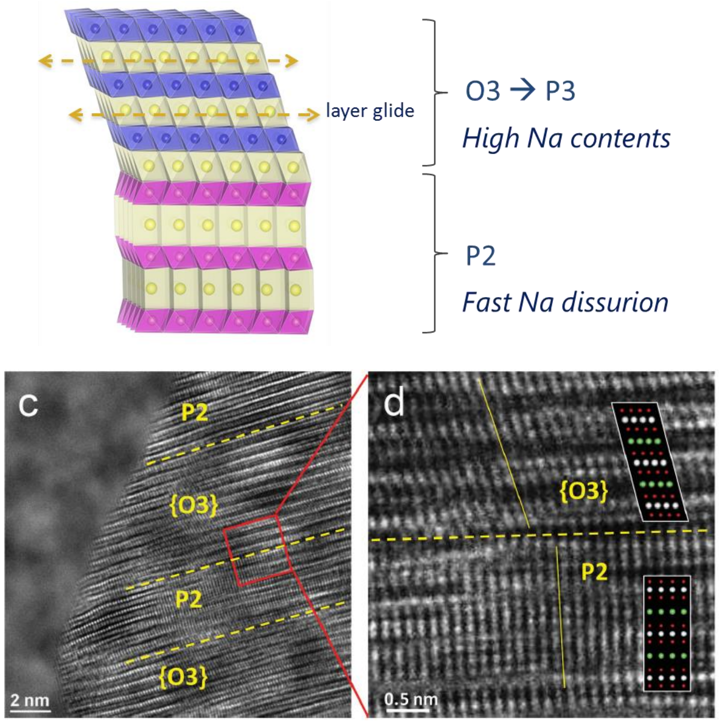


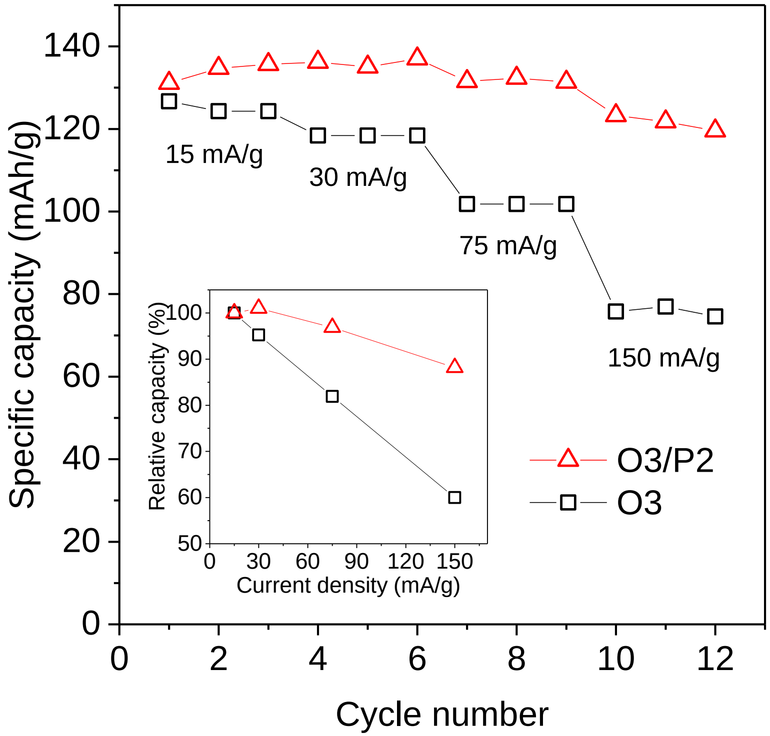
Figure *cycle performance of black phosphorus/Ketjenblack composite.*

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;

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





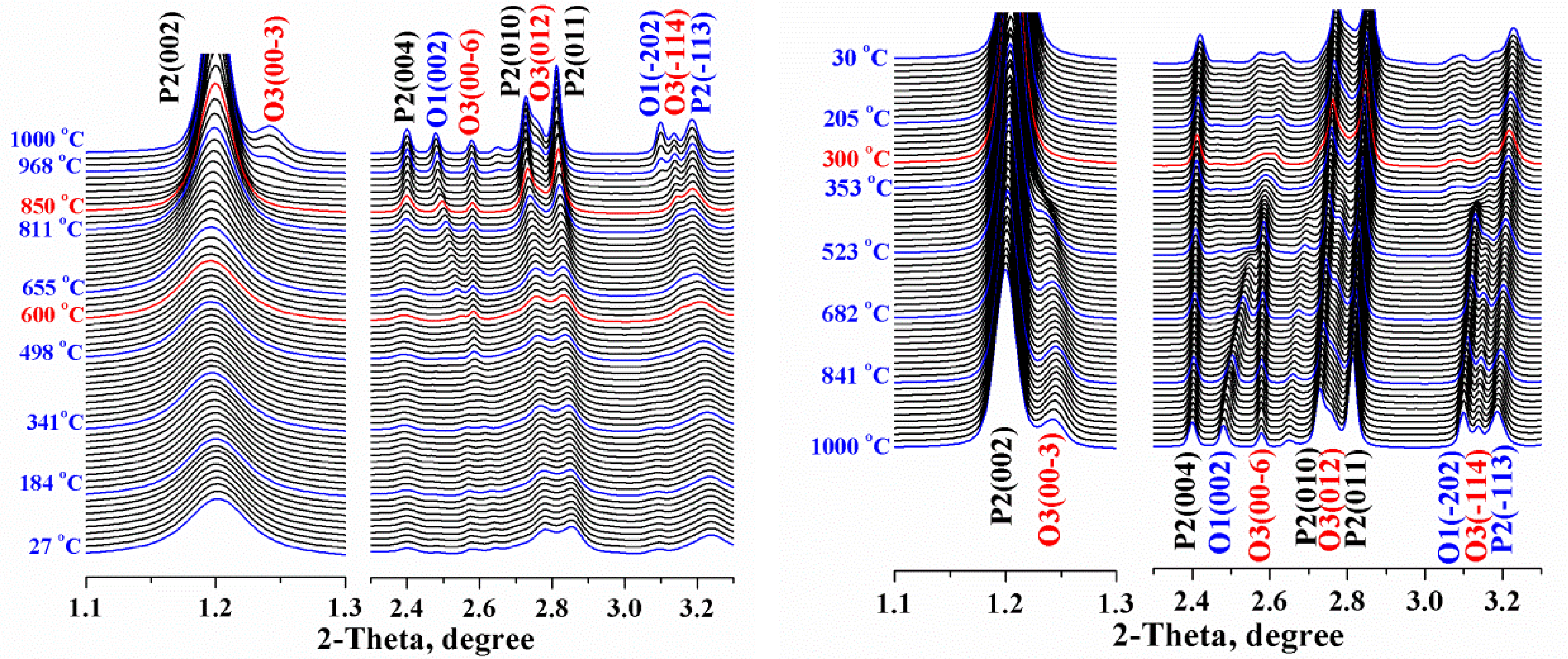
Synergistic performance enhancement mechanism via O3/P2 layer intergrowth structurers was first reported by Argonne team.

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

Cathode work: Understand the sintering process by operando Synchrotron HEXRD

Data from Co-PI, K. Amine

Real-time observation of structure evolution



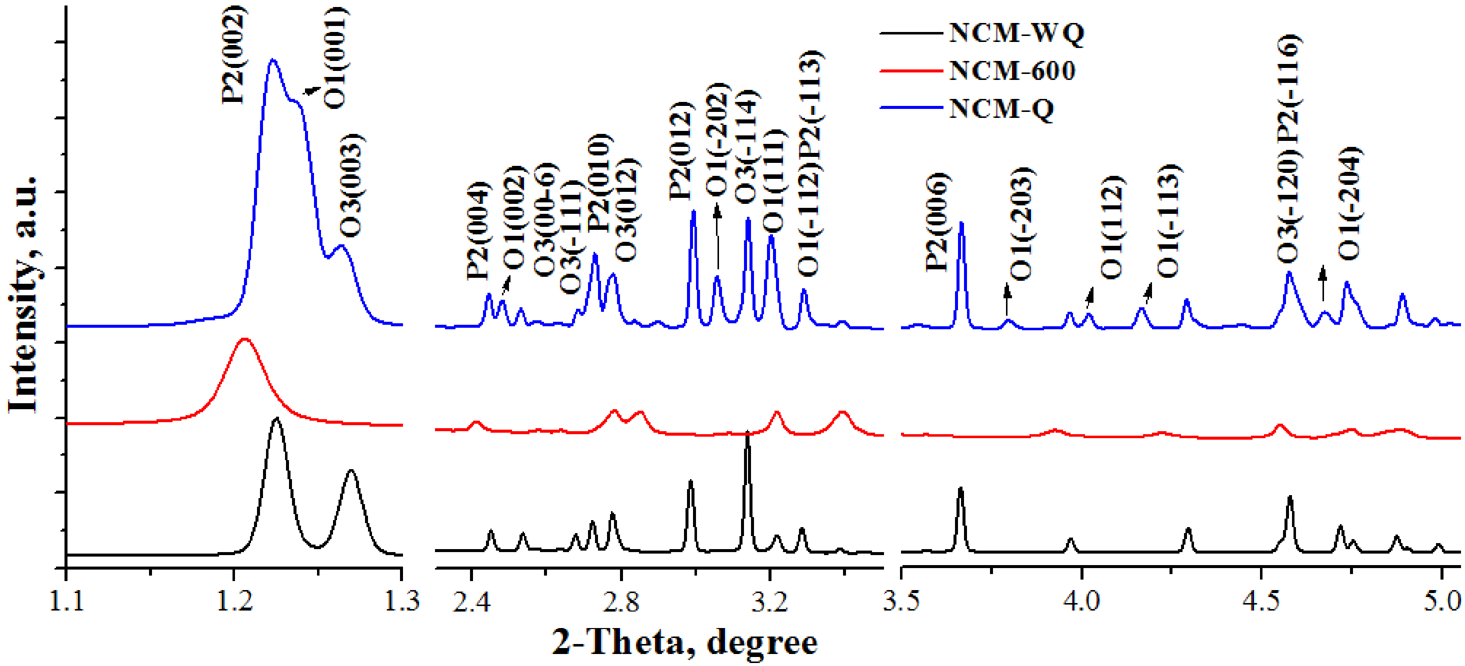
Triple-phase formed at high temperatures;

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

Data from Co-PI, K. Amine

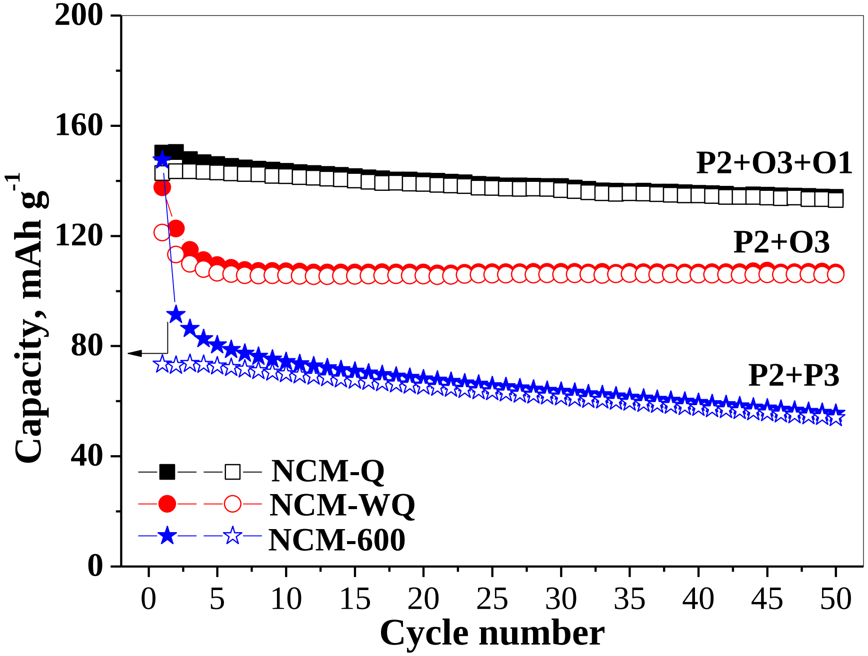


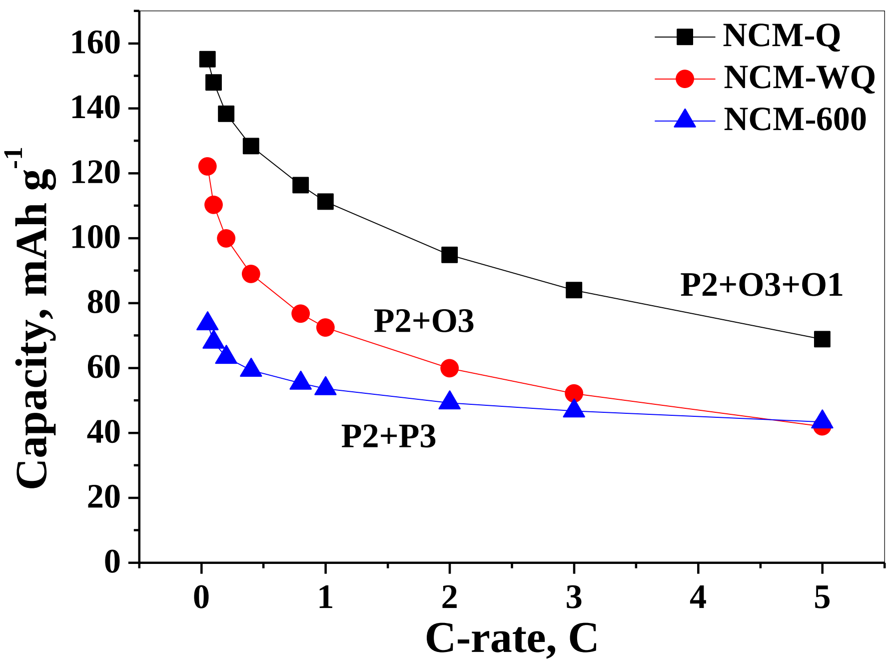
	Structure	Temperature	Time	Heat rate	Cool rate	Quench
NCM-Q	P2+O3+O1	850 °C	12 h	3 °C/min	1 °C/min	Yes
NCM-WQ	P2+O3	850 °C	12 h	3 °C/min	1 °C/min	No
NCM-600	P2+P3	600 °C	10 h	3 °C/min	1 °C/min	No

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

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

Data from Co-PI, K. Amine



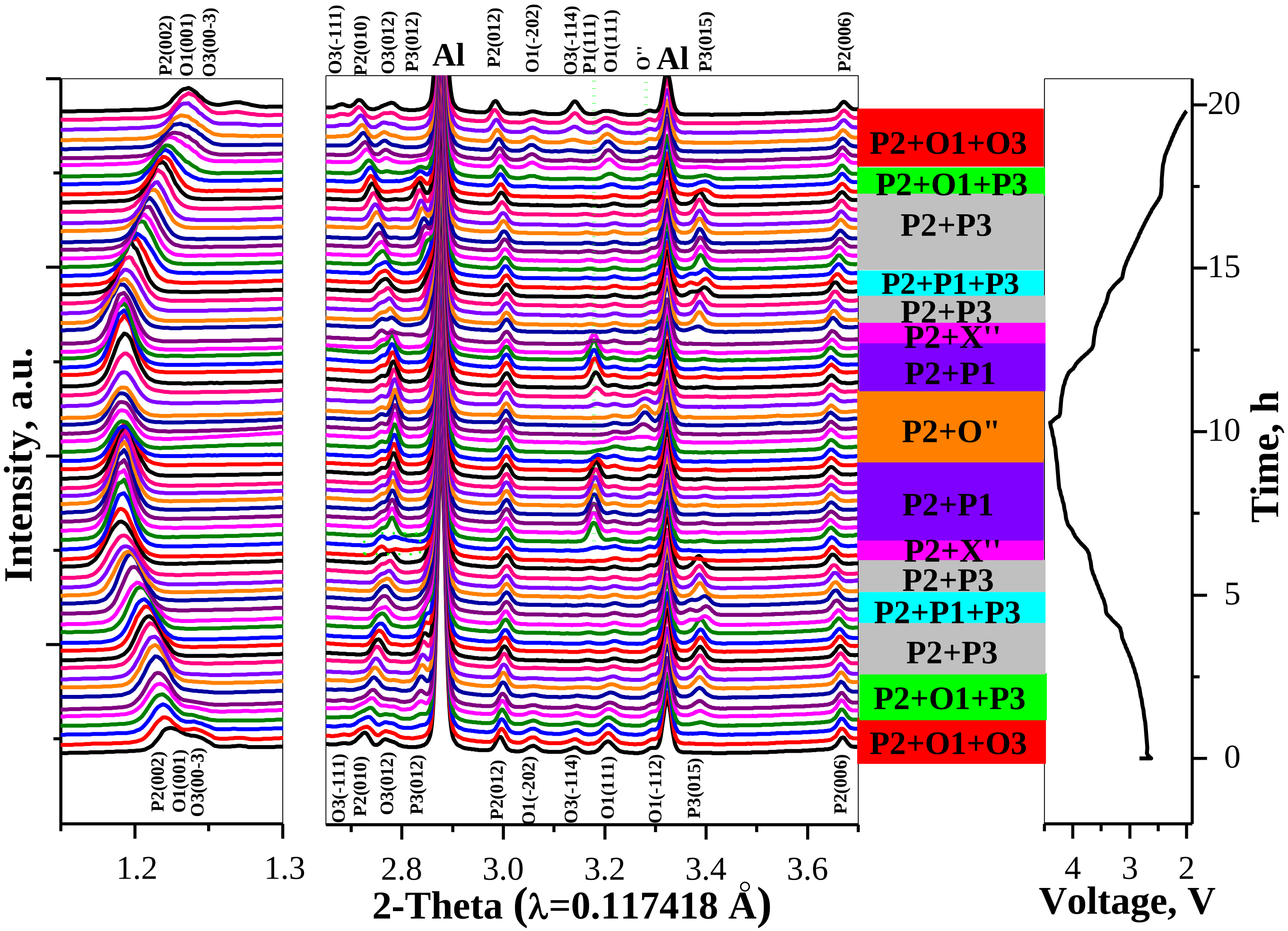


Cycle performance: P2+O3+O1>P2+O3>P2+P3
Rate capability: P2+O3+O1>P2+O3>P2+P3

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

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

Data from Co-PI, K. Amine



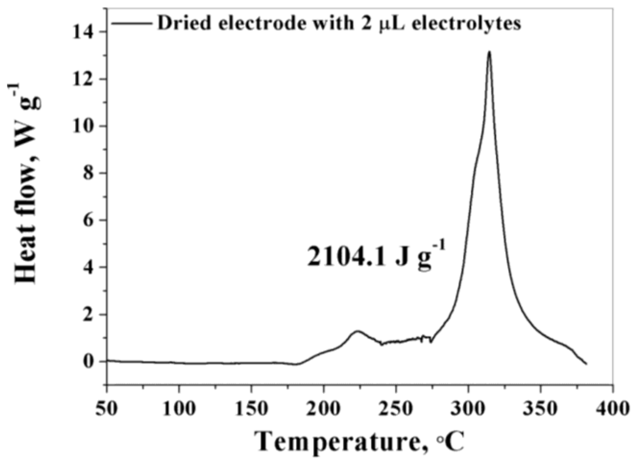
P2 structure is well maintained at deep charge

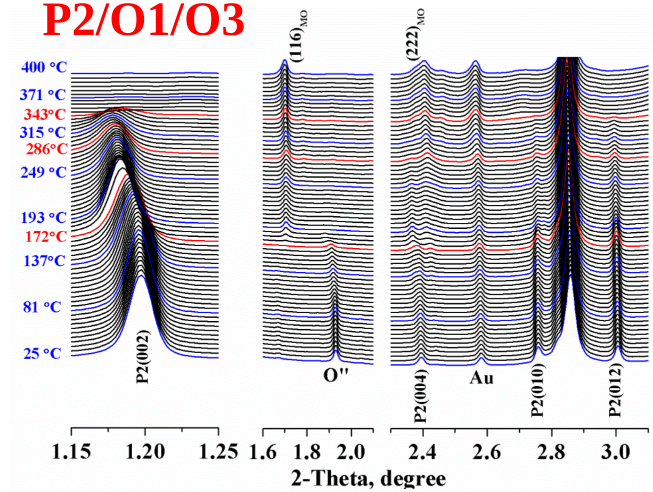
Highly reversible sodiation/de-sodiation for P2/O1/O3 domain

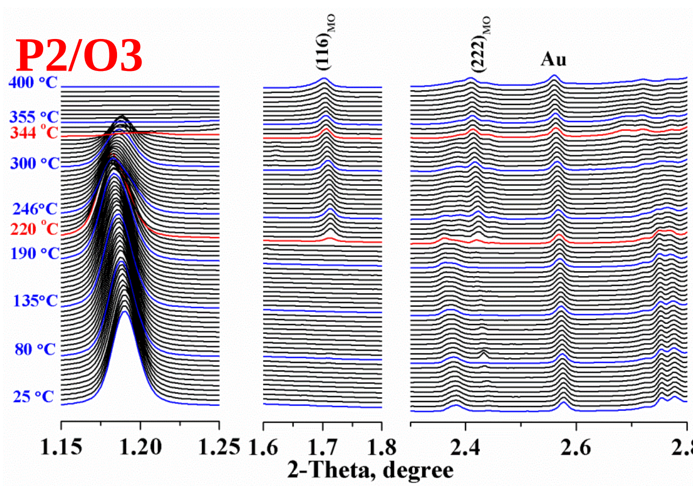
Xu, Chen, Amine et al. *Energy Environ. Sci.* 2017, 10, 1677-1693

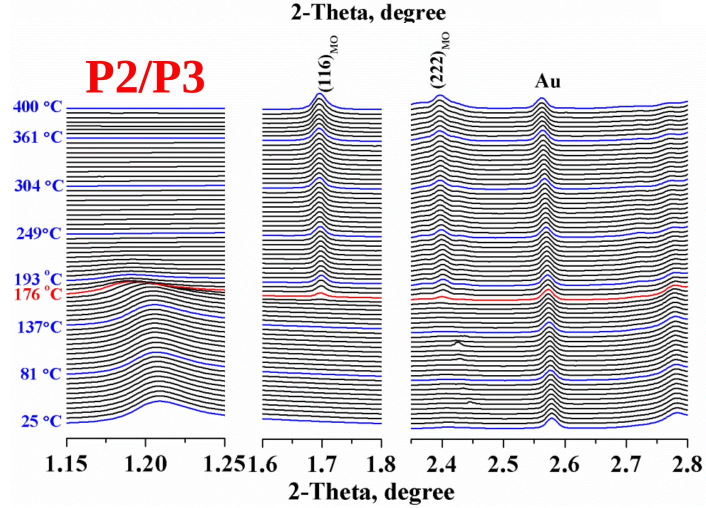
Triple-phase intergrowth structure also improve the thermal stability

Data from Co-PI, K. Amine









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

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Xu, Chen, Amine et al. *Energy Environ. 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, high-performance 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 Fe^{4+} 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