Exploratory Studies of Novel Sodium-ion Battery Systems

Xiao-Qing Yang and Zulipiya Shadike
Brookhaven National Lab. (BNL)

2021 DOE Vehicle Technologies Office
Annual Merit Review

Washington, DC, June 21-25, 2021

BAT287

Overview

Timeline

- Start: 10/01/2020
- Finish: 09/30/2021

Barriers addressed

- To reduce the production cost of a PHEV battery
- Na-ion and Na-metal batteries with long calendar and cycle life
- Na-ion and Na-metal batteries with superior abuse tolerance

Budget

- Funding received in FY20

  DOE: $400k
- Funding received in FY21

  DOE: $320k

Collaborators

- Lawrence Berkeley National Laboratory (LBNL)
- Argonne National Lab. (ANL)
- Pacific Northwest National Lab. (PNNL)
- University of Maryland at College Park
- Harvard University
- Virginia Tech
- Florida State University (FSU)

Relevance and Project Objectives

✓ *To increase the energy density, searching for new cathode materials for Na-ion batteries.*

- Using *in situ* and *ex situ* hard x-ray absorption spectroscopy (hXAS) to study the charge compensation mechanisms of novel P2-type $Na_{0.66}[Mn_{0.61}Ni_{0.28}Sb_{0.11}]O_2$ cathode material for sodium-ion batteries at different state of charges (SOCs).
- Using 2-D XAS mapping and x-ray absorption spectroscopy (XAS, including XANES and XAFS) to study the novel P2-type $Na_{0.66}[Mn_{0.61}Ni_{0.28}Sb_{0.11}]O_2$ cathode material for sodium-ion batteries at different state of charges (SOCs).
- Using synchrotron-based *ex situ* x-ray diffraction (XRD) and Pair Distribution Function analysis (PDF) to study the structure evolution of novel Vacancy-enabled O3 phase stabilization for manganese-rich layered codium Cathode material for sodium-ion during the charge/discharge processes.

✓ *Diagnostics study aimed to improve the calendar and cycle life of batteries.*

- To develop *in situ* and *ex situ* diagnostic techniques with surface and bulk sensitivity to improve the calendar and cycle life of sodium batteries by studying the mechanism of capacity and power fading of Na-ion and Na metal batteries.

✓ *Diagnostics study of electrode materials with lower cost potential.*

BROOKHAVEN NATIONAL LABORATORY

Milestones

Month/Year	Milestones
Dec/2020	Complete x-ray absorption spectroscopy (XAS, including XANES and EXAFS) and two-dimensional (2D) XANES mapping of the pristine P2-$Na_{0.66}[Mn_{0.61}Ni_{0.28}Sb_{0.11}]O_2$ cathode material at Ni and Mn K-edge. ➥ *Completed.*
Mar/2021	Complete Ni and Mn K-edge x-ray absorption spectroscopy (XAS, including XANES and EXAFS) of P2-$Na_{0.66}[Mn_{0.61}Ni_{0.28}Sb_{0.11}]O_2$ cathode material at different state of charges (SOCs) ➥ *Completed.*
Jun/2021	Complete ex-situ TEM, x-ray diffraction (XRD) study and 2D XANES mapping of a high-capacity high-C rate multi-component sodium cathode material with P2 type at different state of charges (SOCs) ➥ *On schedule.*
Sep/2021	Complete Fe, Mn K-edge x-ray absorption spectroscopy (XAS, including XANES and EXAFS) of P2-$Na_{0.7}Mg_{0.2}[Mn_{0.6}Fe_{0.2}\square_{0.2}]O_2$ cathode material at different state of charges (SOCs). ➥ *On schedule.*

BROOKHAVEN NATIONAL LABORATORY

Approaches

- Synchrotron based *in situ* and *ex situ* x-ray diffraction (XRD) techniques to study the phase transition and structural changes of cathode materials for Na-ion batteries during charge-discharge cycling
- Synchrotron based x-ray absorption spectroscopy (XAS), combined with spatially resolved 2-D x-ray fluorescence (XRF) mapping to study the redox mechanism of cathode materials of Na-ion batteries.
- Synchrotron based x-ray pair distribution function analysis (xPDF) to elucidate the long and short range ordering of cathode materials for Na-ion batteries.
- Extended collaboration with other US and international academic institutions and US industrial partners.

Synchrotron X-ray based techniques for sodium battery studies

23-ID-2 and 7-ID-1 @NSLS-II

18-ID and 3-ID @NSLS-II

Soft X-ray absorption spectroscopy (sXAS)

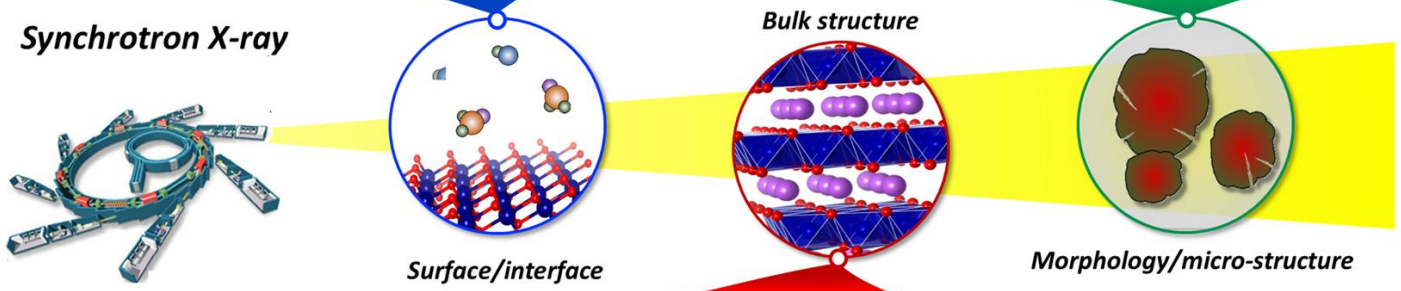
- Extremely surface sensitive
- Different modes with different probing depth
  - Auger electron yield (AEY): ~ 1nm
  - Total electron yield (TEY): ~10nm
  - Partial electron yield (PEY): ~5nm
  - Total fluorescence yield (TFY): ~ 500nm

- Requires UHV condition : limit in situ capability for liquid electrolyte

Scanning/Transmission X-ray microscopy (STXM/TXM)

- Morphology and micro-structure evaluation in micro/meso/macro scale
: Micro-crack, particle fracture, tortuosity

- Chemical information (elemental/chemical mapping)
: concentration gradient, oxidation state in single/multiple particle level (chemical inhomogeneity)



X-ray diffraction (XRD)

- Average crystal structure (long-range order)
  - Lattice parameter
  - Phase
  - Strain
  - Atomic position
  - Site occupancy
  - Texture
  - Stacking faults

Pair distribution function (PDF)

- Total scattering (Bragg+diffuse scattering)
- Local structure information
: Inter-atomic distance, coordination numbers

- Cover middle range structure between XRD and EXAFS

Hard X-ray absorption spectroscopy (XAS: XANES and EXAFS)

- Valence state changes during electrochemical reaction
: revealing charge compensation mechanism in elemental specific way
- Coordination environment (e.g., octahedral, tetrahedral etc.)
- Local structural changes
: bond length, degree of disorder

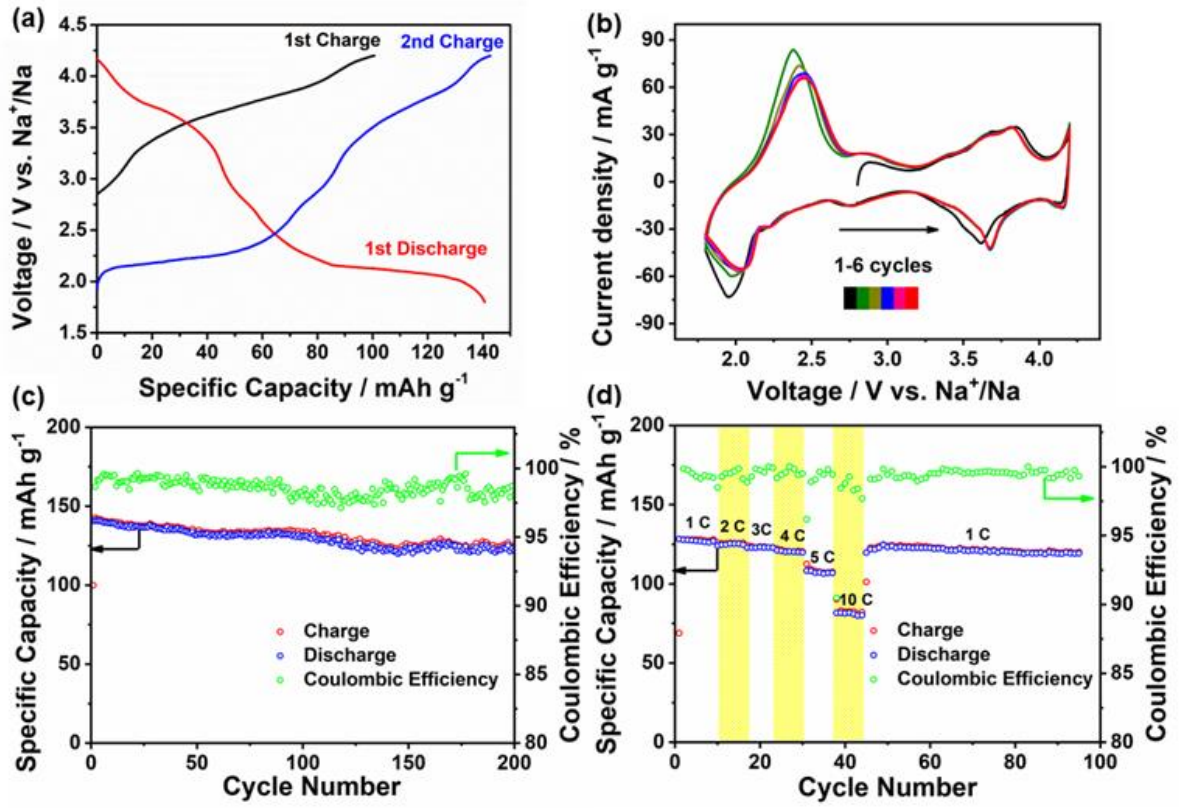
28-ID-2@NSLS-II

28-ID-1@NSLS-II

8-ID and 7-BM@NSLS-II

Technical Accomplishments

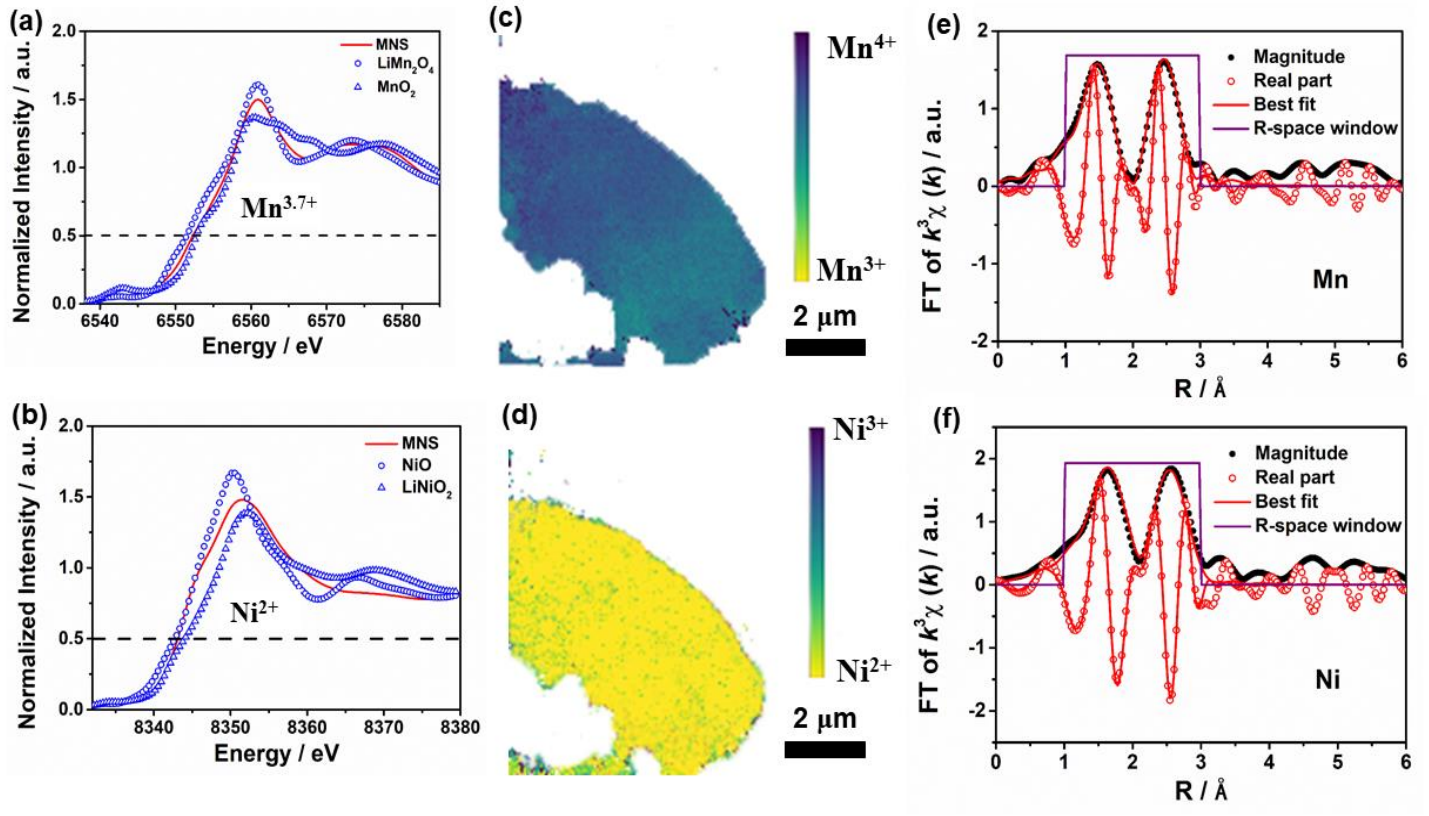
Electrochemical performance of P2-type $Na_{0.66}[Mn_{0.61}Ni_{0.28}Sb_{0.11}]O_2$ (NMS)cathode material



- Galvanostatic charge/discharge curves of MNS at a cur-rent rate of 0.1 C (14 mAh g_{-1}) at voltage range between 1.8-4.2 V. b) CV curves of MNS at 0.1 mV s_{-1} at voltage range from 1.8-4.2 V. c) Cycling performance at 0.5 C for 200 cycles and d) rate ability at current rate increasing from 1 C to 10 C and return to 1 C.

Technical Accomplishments

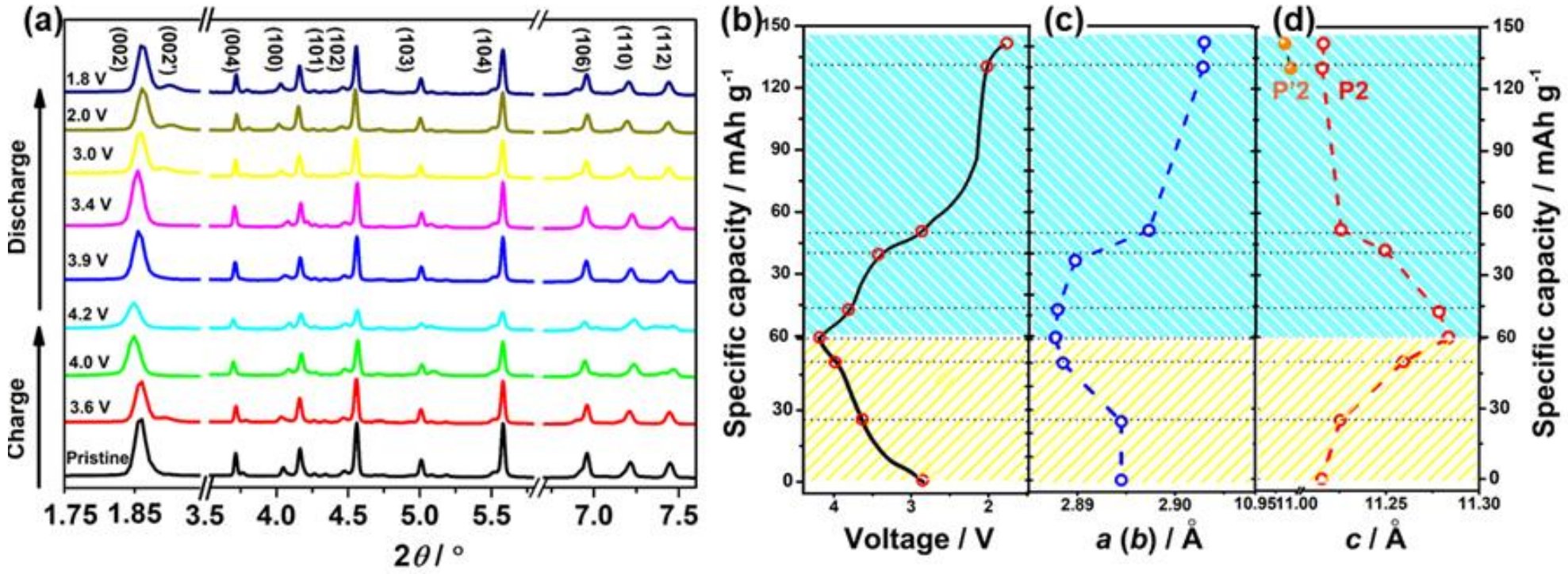
XANES spectra and 2D XANES mapping of $Na_{0.66}[Mn_{0.61}Ni_{0.28}Sb_{0.11}]O_2$ (NMS) cathode material



- XANES spectra of the a) Mn and b) Ni K-edges of pristine MNS and standard metal oxide references. The two-dimensional (2D) XANES mapping of c) Mn and d) Ni in MNS. The least-square fits of the calculated FT-EXAFS phase and amplitude functions to the experimental EXAFS spectra for Mn e) and Ni f) in MNS.

Technical Accomplishments

Ex situ XRD patterns of MNS electrodes during the first charge and discharge

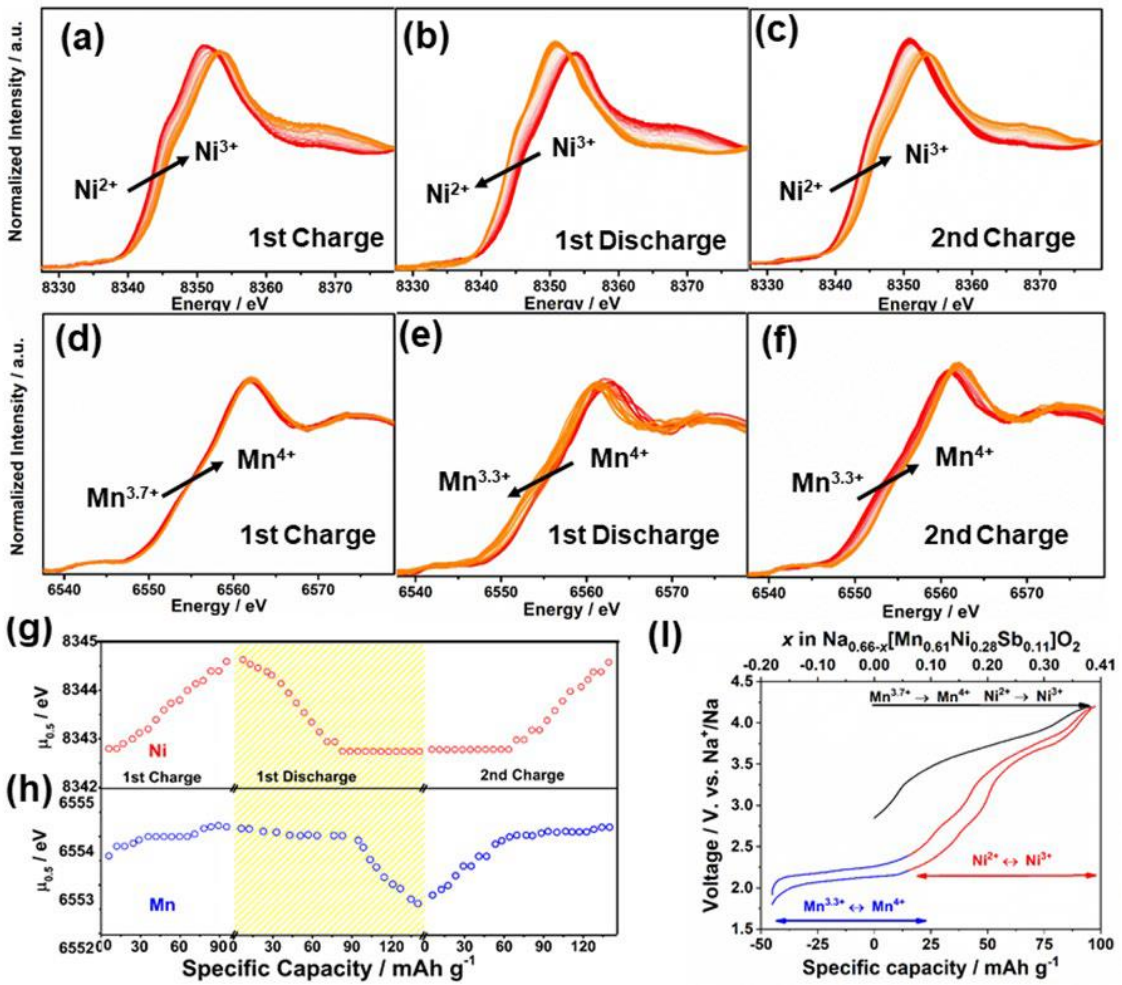


Energy (eV) Energy (eV) Energy (eV)

- a) Ex situ synchrotron-based XRD patterns of MNS electrodes during the first charge and discharge processes (X-ray wavelength = 0.18208 Å). b) Corresponding voltage profiles during XRD data collection. c) and d) The evolution of the lattice parameter a(b) and c as function of the specific capacity

Technical Accomplishments

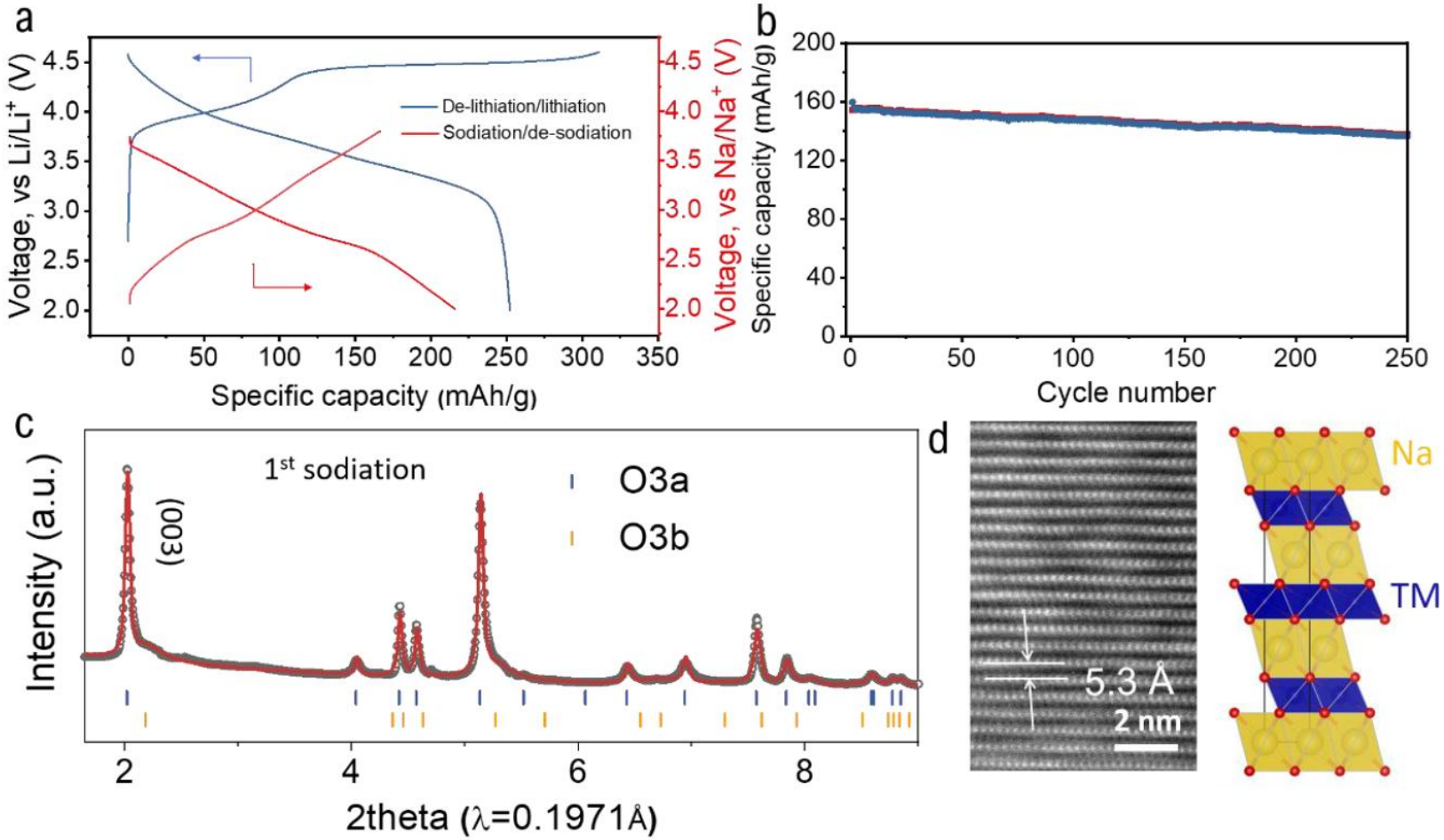
In situ XAS spectra of MNS during the initial charging-discharge and 2nd charge



- In situ XAS spectra for MNS. a-c) Ni and d-f) Mn K-edge XANES of MNS at various stages during the first charge/discharge and second charge processes, respectively. The edge energy evolution at half edge-step ($E_{0.5}$) for Ni g) and Mn h) in $Na_{0.67}[Mn_{0.61}Ni_{0.28}Sb_{0.11}]O_2$ at different states. i) Charge compensation of different elements contribution during charge and discharge.

Technical Accomplishments

Electrochemical performance and structure studies of $Li_{1.2}[Mn_{0.66}Co_{0.17}Ni_{0.17}]_{0.8}O_2$ (LRNMC) and Vacancy-enabled O3 phase $Na_{1-x}Li_x[(Mn_{0.66}Co_{0.17}Ni_{0.17})_{0.8}\square_{0.2}]O_{2-y}$ (NaLRNMC)



- (a) Curves of de-lithiation to 4.6V (LRNMC4.6), lithiation to 2V, sodiation of LRNMC4.6 to 2V (NaLRNMC4.6) and its de-sodiation to 3.8 V. (b) Cycling performance of NaLRNMC4.6 at125 mA/g. (c) ex-situ synchrotron XRD of NaLRNMC4.6 after 1st sodiation (λ =0.1971(1)Å). (d) HAADF image of the NaLRNMC4.6 after 1st sodiation.

Technical Accomplishments

- Through collaboration with scientists at PNNL, ANL, Harvard University, Virginia Tech, FSU, and Stanford University, the structural changes of vacancy-enabled O3 phase $Na_{1-x}Li_x[(Mn_{0.66}Co_{0.17}Ni_{0.17})_{0.8}\square_{0.2}]O_{2-y}$ (NaLRNMC) cathode material during electrochemical cycling were studied using synchrotron-based XRD and X-ray absorption near edge spectroscopy (XANES) and Extended X-ray absorption find structure spectroscopy (EXAFS). The results of this study were published on ***Angew. Chem. Int. Ed*** in January 2021.
- Through collaboration, charge compensation mechanism of novel P2-type $Na_{0.67}[Mn_{0.61}Ni_{0.28}Sb_{0.11}]O_2$ cathode material has been studied using *synchrotron-based* XANES and EXAFS spectroscopy, the results was published on ***Advanced Energy Materials (AEM)*** in February 2021.
- Through collaborations whole-voltage-range oxygen redox in P2-Layered cathode materials $Na_{0.7}Mg_x[Fe_{0.4-x}Mn_{0.6}\square_x]O_2$ (□ denotes a vacancy) for sodium-ion batteries has been studied. Results were published on ***Advanced Materials*** in March 2021.

Collaborations with other institutions and companies

- Lawrence Berkeley National Laboratory (LBNL)
- Argonne National Lab. (ANL)
- Pacific Northwest National Lab. (PNNL)
- University of Maryland at College Park
- Harvard University
- Virginia Tech
- Florida State University (FSU)

BROOKHAVEN NATIONAL LABORATORY

Proposed Future Work for *FY 2021* and *FY2022*

▣ **FY2021 Q3 Milestone:**

Complete ex-situ TEM, x-ray diffraction (XRD) study and 2D XANES mapping of a high-capacity high-C rate multi-component sodium cathode material with P2 type at different state of charges (SOCs)

▣ **FY2021 Q4 Milestone:**

Complete Fe, Mn K-edge x-ray absorption spectroscopy (XAS, including XANES and EXAFS) of P2-$Na_{0.7}Mg_{0.2}[Mn_{0.6}Fe_{0.2}\square_{0.2}]O_2$ cathode material at different state of charges (SOCs).

FY2022 work proposed:

- ▣ **Synchrotron based *in situ* and *ex situ* XRD and XAS techniques will be applied to study the structural stability and charge compensation mechanisms of new cathode materials $Na(CuMn)O_2$ and $Na(NiMn)O_2$ for Na batteries.**
- ▣ **Synchrotron based *ex situ* XAS techniques will be applied to study the structure evolution and charge compensation mechanisms of P2-type layered $Na_{0.75}Mn_{0.5}Fe_{0.15}Mg_{0.25}O_2$ and $Na_{0.8}Mg_{0.22}Fe_{0.25}Mn_{0.53}O_2$ cathode material for Na batteries.**
- ▣ **The collaborative research with US academic research institutions and industrial partners will be further expanded and strengthened.**

Summary

Relevance

- ✓ *To increase the energy density, searching for new cathode materials for Na-ion batteries.*
- ✓ *Diagnostics study aimed to improve the calendar and cycle life of batteries.*
- ✓ *Diagnostics study of new electrode materials with lower cost potential.*

Approaches

- *In situ and ex situ x-ray diffraction and absorption spectroscopy*
- *Synchrotron based x-ray pair distribution function (XPDF)*
- *2D X-ray fluorescence (XRF) mapping*
- *Synchrotron based transmission x-ray microscopy (TXM)*

Technical Accomplishments

- *Structural changes of vacancy-enabled O3 phase $Na_{1-x}Li_x[(Mn_{0.66}Co_{0.17}Ni_{0.17})_{0.8}\square_{0.2}]O_{2-y}$ (NaLRNMC) cathode material during electrochemical cycling have been studied . (Angew. Chem. Int. Ed 2021)*
- *Charge compensation mechanism of novel P2-type $Na_{0.67}[Mn_{0.61}Ni_{0.28}Sb_{0.11}]O_2$ cathode material has been studied using ex situ XANES and EXAFS spectroscopy. (Advanced Energy Materials, 2021)*
- *P2-Layered cathode materials $Na_{0.7}Mg_x[Fe_{0.4-x}Mn_{0.6}\square_x]O_2$ ($\square$ denotes a vacancy) for sodium-ion batteries has been studied. (Advanced Materials in March 2021).*

Proposed Future work

- *Synchrotron based in situ and ex situ XRD and XAS techniques will be applied to study the structural stability and charge compensation mechanisms of new cathode materials $Na(CuMn)O_2$ and $Na(NiMn)O_2$ for Na-ion batteries.*
- *Synchrotron based ex situ XAS techniques will be applied to study the structure evolution and charge compensation mechanisms of P2-type layered $Na_{0.75}Mn_{0.5}Fe_{0.15}Mg_{0.25}O_2$ and $Na_{0.8}Mg_{0.22}Fe_{0.25}Mn_{0.53}O_2$ cathode material for Na-ion batteries.*