Status and Challenges of Electrode Materials for High Energy Cells

Presented by

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2020 DOE Vehicle Technologies Program Review

June 4th, 2020

Project ID # bat359

BATTERY 500 CONSORTIUM

OVERVIEW

Timeline

- Project start date: 10-01-2016
- Project end date: 9-30-2021
- Percent complete: 70%

Budget

- Total project funding
  - DOE $50M
  - Contractor share: Personnel
- Funding received
  - FY19: $10M
  - FY 20: $10M

Barriers

- Barriers addressed
  - High energy density of 500 Wh/kg
  - Abuse-tolerant safer electrodes
    - Energy vs Safety
  - Cycle life

Partners

- Project Lead
  - PNNL
- National Laboratories
  - PNNL, INL, Brookhaven, SLAC/Stanford
- Academia
  - UC San Diego, U. Washington, U. Texas

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RELEVANCE

- **Overall Battery 500 Objective**
  - Develop commercially viable Li battery technologies with a cell level specific energy of 500 Wh/kg through innovative electrode and cell designs that enable utilization of maximum capacity of advanced electrode materials
- **Chemistry**
  - Utilize a L**i metal anode** combined with a compatible electrolyte system, and either
    - **A nickel-rich NMC** or S
- **Keystone project (1): Materials and Interfaces**
  - Provides the materials and chemistry support for Keystone projects
    - (2) Electrode Architecture, and
    - (3) Cell Design and Integration

MILESTONES: KEYSTONE 1 and BINGHAMTON

End date	12/31/2019	03/31/2020	06/30/2020	09/30/2020
Type	Quarterly Q1	Quarterly Q2	Quarterly Q3	Quarterly Q4
Keystone Project 1 Materials and Interfaces	Select an effective approach for coating NMC cathode materials and improve cathode stability for B500. Completed	Recommend methods to mitigate first cycle life of high Ni NMC materials. Completed	Validate dual diluent electrolytes stable for both cathodes and anodes. On Track	Preparation of high-Ni (Ni>0.8) layered oxide cathodes that are capable of delivering > 220 mA h g^{-1} with > 80% capacity retention over 200 cycles. On Track
Binghamton	Identify the cause of first cycle loss of high Ni NMC materials. Completed	Recommend methods to mitigate first cycle life of high Ni NMC materials. Completed	Provide a critical analysis of progresses in high energy batteries from industry or other research groups. On Track	Report on thermal stability study of Ni-rich cathodes, and initiate study on Li/electrolyte reactions On Track

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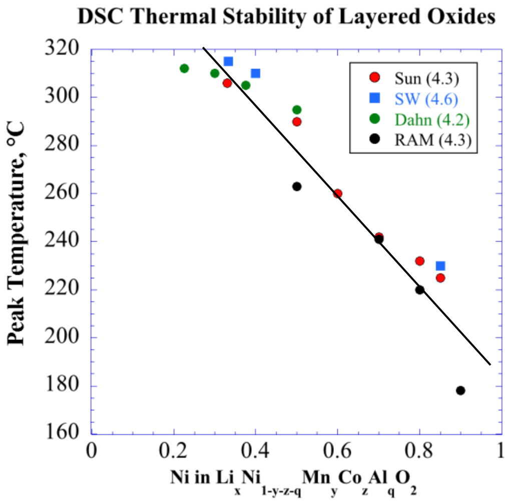
KEYSTONE 1 CHALLENGES AND APPROACH – NMCA

- **How to handle the capacity vs stability challenge**
  - Evaluate different compositions
    - Used **622** as initial baseline, against which materials are compared
    - Used to meet Years 1-3 full cell milestones, now 350 Wh/kg *(PNNL)*
  - Evaluated and recommended **811** for 2nd generation, for 400Wh/kg
    - 622 and 811 obtained commercially *(BU/UCSD)*
  - Build synthesis capability for **higher Ni** within the consortium *(Texas)*
    - Allows Ni contents over 90% to be obtained and tested
  - Determine the key limitations and how to mitigate them
    - **1st cycle loss,** surface reactivity; morphology, **coatings** *(UW, BU, UCSD)*
  - Build stability characterization facility *(BU)*
    - Allows evaluation of side reactions and thermal stability while cycling cells
    - Evaluate the poor environmental stability of the highest Ni materials
  - Develop **new electrolytes** that have greater stability to NMC and Li metal *(PNNL)*
  - Build characterization techniques to study materials at the atomic level *(BNL/UCSD)*
    - Determines atom migration and material degradation



Capacity increasing
Reactivity increasing

KEYSTONE 1 CHALLENGES AND APPROACH – Li and S

- **How to plate lithium metal smoothly without dendrites**
  - Evaluate SEI formation and effectiveness
    - Use cryo-EM to visualize nanostructure of deposition *(UCSD)*
    - Use x-ray operando studies to follow degradation of lithium *(SLAC)*
  - Develop artificial SEI layers
    - Organic: Polymeric self-healing SEI films *(Stanford)*
    - Inorganic: LiF film formed from graphite fluoride *(Texas)*

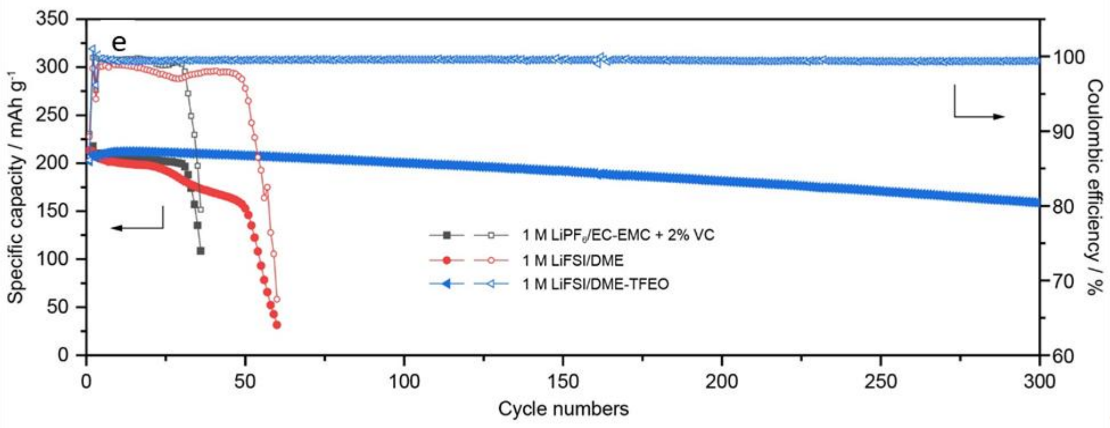
- **How to control and fully use the sulfur cathode to allow high mass loadings**
  - Evaluate redox mediators *(Stanford)*
    - To reduce overpotential on charging
    - To allow full utilization of Li_2S
  - Find new electrolytes *(PNNL)*

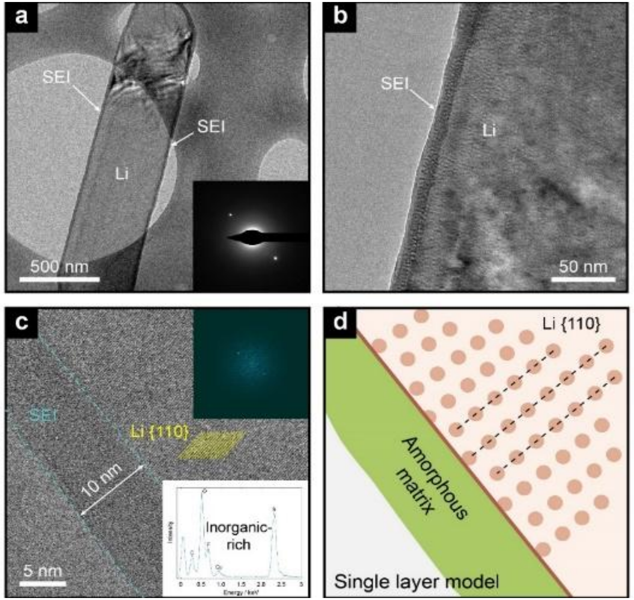
MILESTONE: IDENTIFY NEXT GENERATION ELECTROLYTES

Project ID # bat429

Localized high concentration electrolyte (LHCE) developed

- Hydrofluoroorthoformate based LHCE is 1 M LiFSI in DME-TFEO
  - High boiling point of the TFEO diluent enhances stability
- Coulombic efficiency over 99.5%
  - Forms stable SEI on Li
  - Less expansion on extended cycling
- Works well with NMC 811

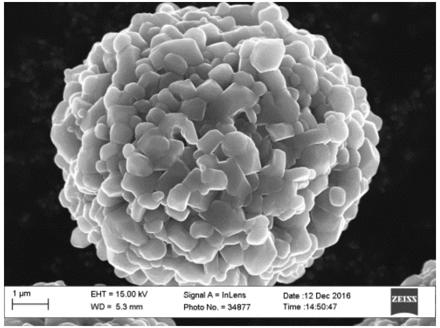


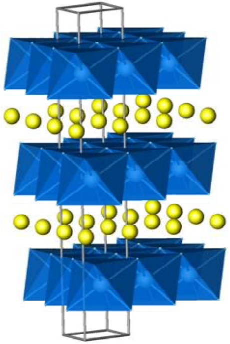


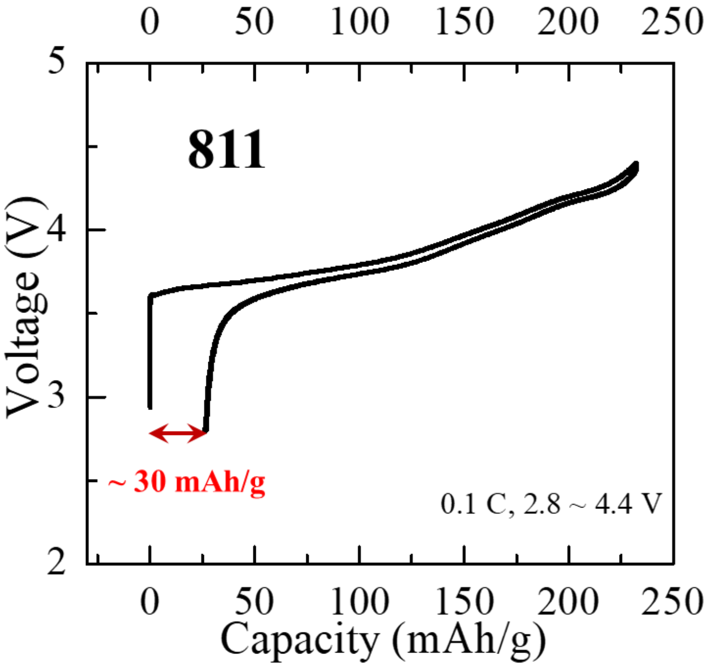
MILESTONE: IDENTIFY THE CAUSE OF THE 1ST CYCLE LOSS

Today ~ 12% capacity loss on 1st cycle

- If eliminated allows:
  - 400-500 Wh/kg cells
  - 1000 Wh/l



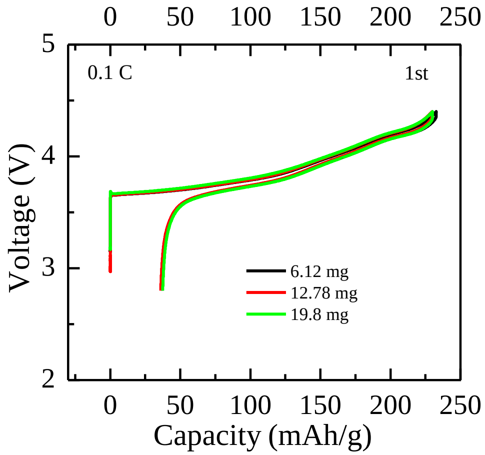




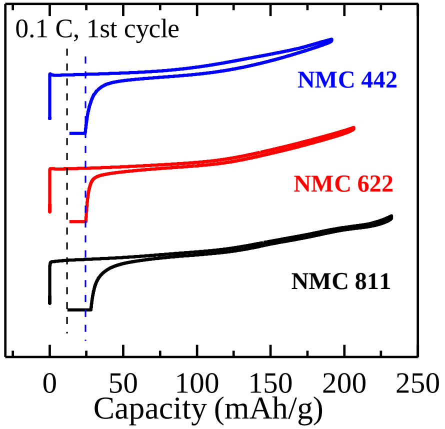
MANY PARAMETERS NOT IMPORTANT FOR 1ST CYCLE LOSS

Loading of active material

811

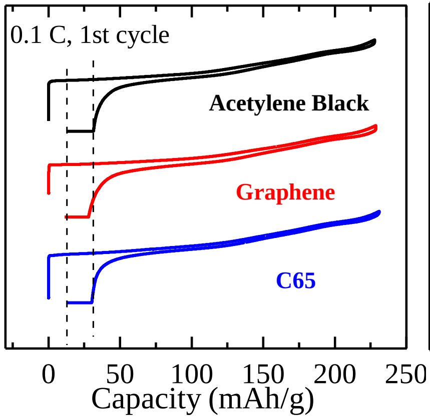


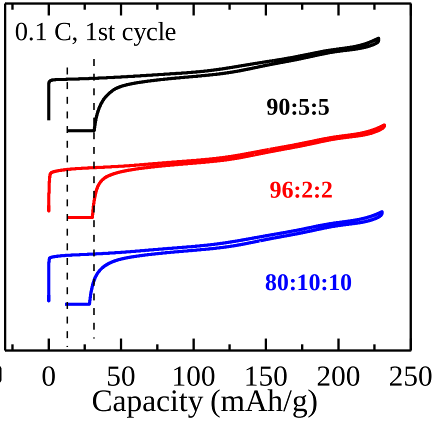
Ni content



C type and amount

811





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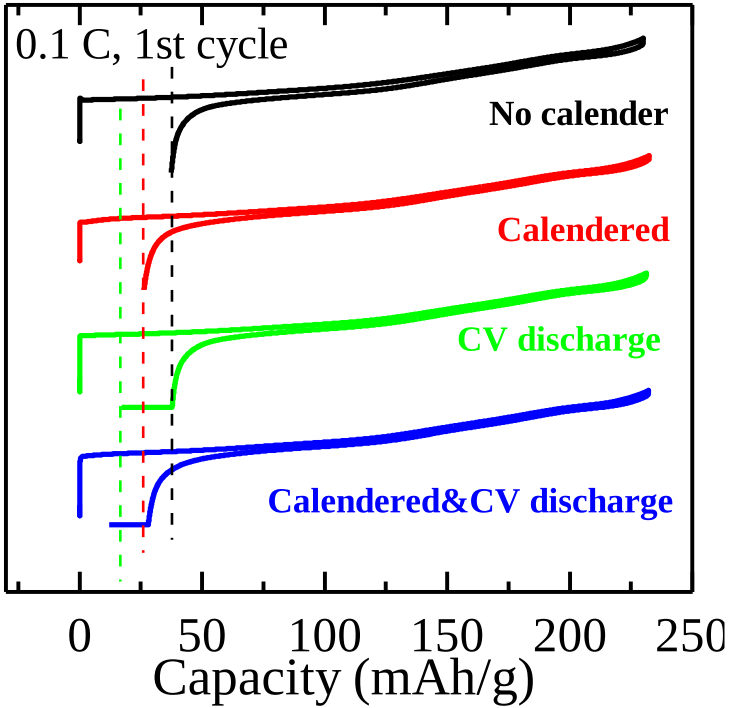
CALLENDERING AND CC/CV DISCHARGE REDUCE 1ST CYCLE LOSS

Callendering has a positive impact impact

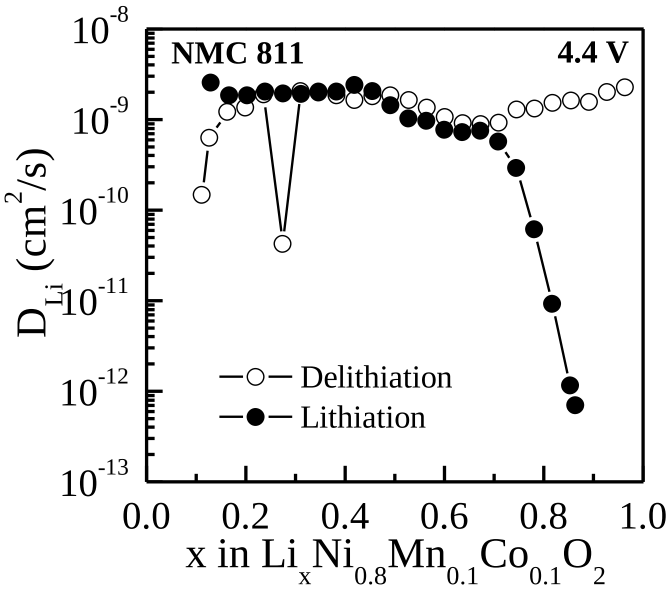


Clues to cause of loss:

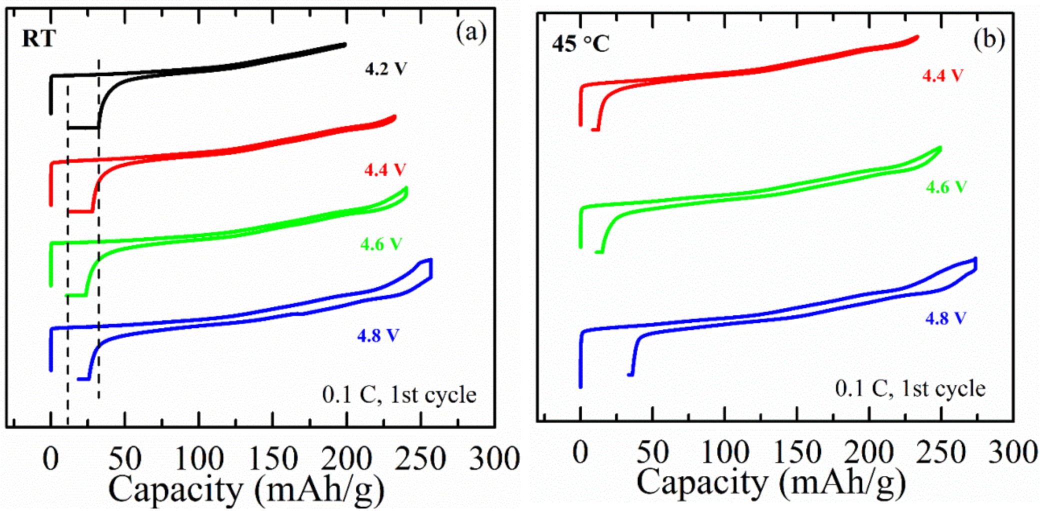
- mAh/g loss is essentially the same
  - Independent of depth of charge *(UCSD)*
- Suggests last 10% of Li controls
- CC/CV discharge recovers some loss
  - Suggests slow **kinetics** at high Li

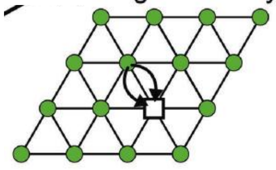
1^{ST} CYCLE LOSS APPEARS TO BE DUE TO SLOW Li DIFFUSION

Diffusion falls fast at high [Li]



Raising the **temperature** reduces the loss





But, why does $LiCoO_2$ have a much lower 1st cycle loss?

- Study underway
- **Lattice substitution or coating** might help

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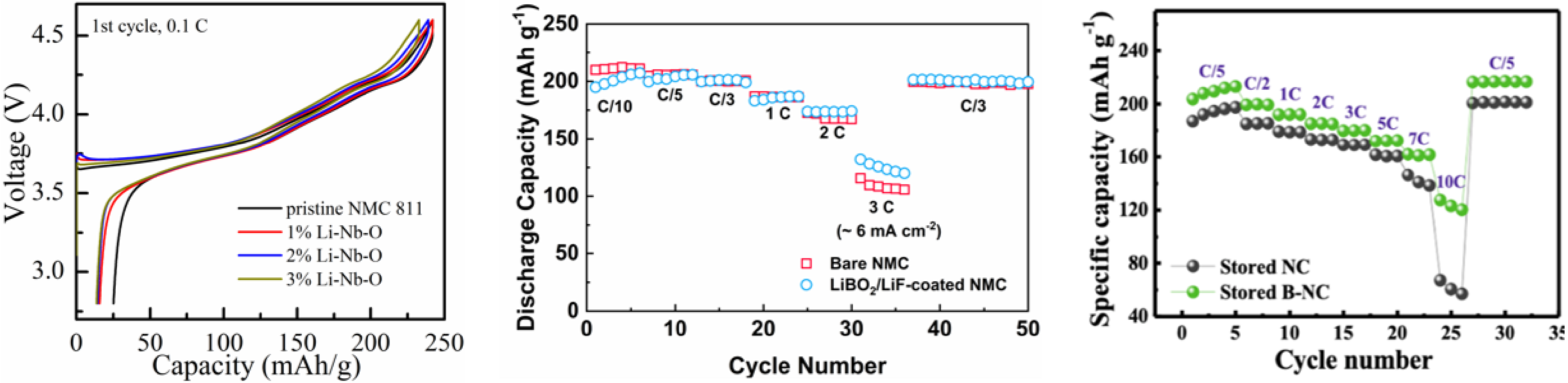
MILESTONE: IDENTIFY EFFECTIVE COATING APPROACH FOR NMC



(Left) 1st cycle behavior of NMC811 in voltage range 2.8-4.6 V; (middle) rate capability of NMC811 with a $LiBO_2$/LiF coating in voltage range 2.8-4.6 V, and (right) rate capability of $LiNi_{0.94}Co_{0.06}O_2$ after storage in voltage range 2.8-4.4 V.

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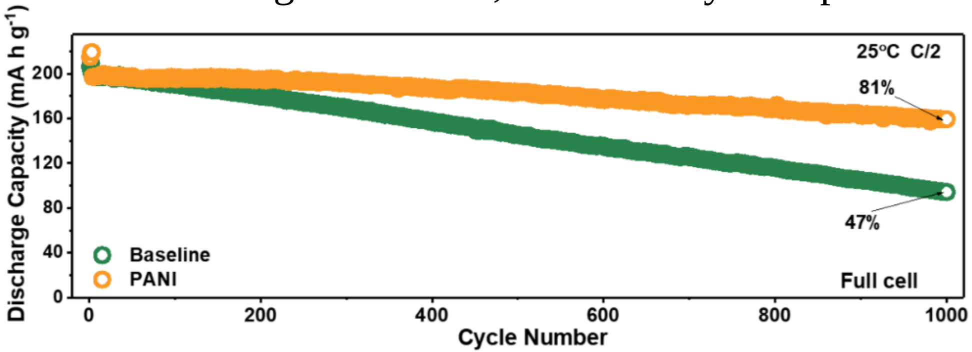
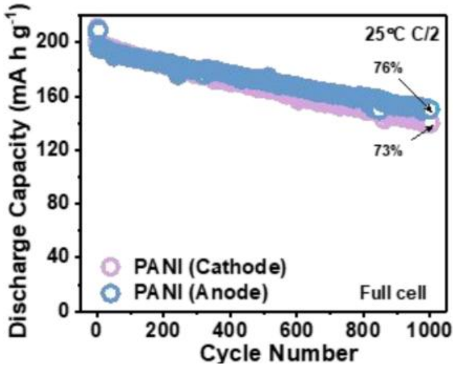
MILESTONE: SYNTHESIS AND CHARACTERIZATION OF Ni>0.8 NMC

- **$LiNi_{0.9}Mn_{0.05}Co_{0.05}O_2$ NMC** successfully synthesized
- Conductive polymer polyaniline (PANI) used as additive/binder. 5:1 PANI:PDVF
  - In both electrodes
    - Excellent cycling vs a graphite anode
      - May be an HF scavenger
    - Capacity retention improved from 47% to 81% after 1,000 cycles
    - Improved coulombic efficiency, 99.5 vs 98.5% without PANI
    - Improved discharge voltage, (3.6 V vs. 3.2V at 1,000 cycles).
  - Even in a single electrode, cell stability is improved

Project ID # bat360





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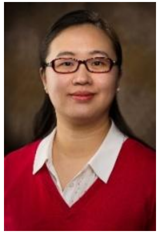
RESPONSE TO 2018/2019 REVIEWERS' COMMENTS

No Reviewer Comments

BU COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- **National Laboratories**
  - PNNL, INL and BNL
    - Pouch cell studies
    - Experimental input to system modeling
    - Synchroton: Ex-situ and operando synchrotron X-ray diffraction,
    - Neutron diffraction



- **Academia**
  - UC San Diego, UT Austin and U. Washington:
    - Ni-rich NMC synthesis and characterization, doping/coating, in-situ XRD
    - Experimental input to UW modeling



- **Industry**
  - Working through NYBEST and NAATBaat to disseminate information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REMAINING CHALLENGES AND BARRIERS FOR NMCA – KEYSTONE 1

- **The Safety Trade-off: Energy vs Thermal Stability**
  - Increasing Ni content increases capacity
  - Increasing Ni content decreases thermal stability
  - Increasing Ni content and/or higher charging voltage increases capacity fade
- **Capacity Improvement**
  - Need to extract > 220 Ah/kg to achieve 500 Wh/kg cells
    - Reduce 1st cycle loss, and increase Ni content
- **Capacity Retention**
  - The surface must be stabilized against reaction with the electrolyte
  - Metal dissolution must be eliminated
  - Cracking and other mechanical degradation must be minimized
    - Meat balls vs separate crystals
- **Thicker Electrodes needed to decrease inactive weight**
  - Will need improved ionic conductivity in the $LiMO_2$
  - Will need enhanced electrode electronic conductivity

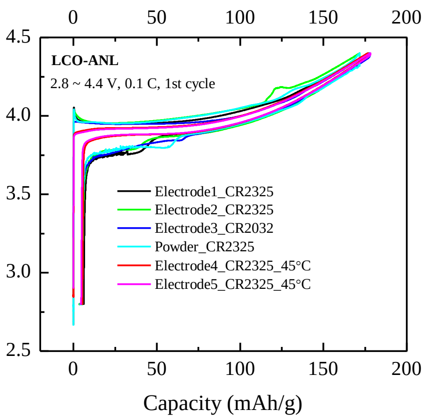
PROPOSED FUTURE WORK – KEYSTONE 1 – Li/NMCA

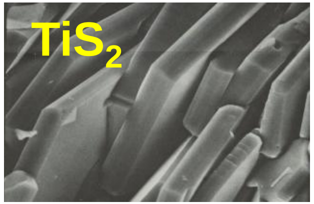
- **Push the high Ni and low Co limits of NMCA**
  - Gassing
  - Thermal stability (DSC et al)
  - Capacity fading

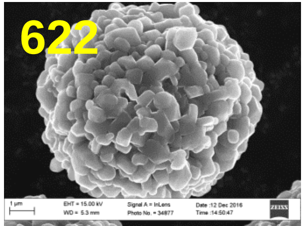
- **Evaluate options for increasing conductivity**
  - Ionic and electronic, to allow thicker electrodes

- **Evaluate options for improving Capacity Retention**
  - Minimize 1^{st} cycle loss
    - Understand why LCO has minimal loss
  - Develop even better electrolytes, for Li and NMC
    - Emphasize Li, as it is now the limiting component
  - Determine role of doping in the lattice and/or surface coatings
  - Evaluate meat balls vs separate crystals

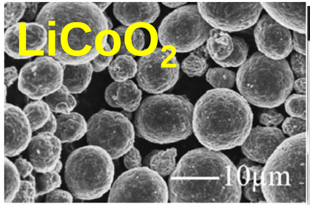
- **Provide technical support to Keystone 2 and 3**

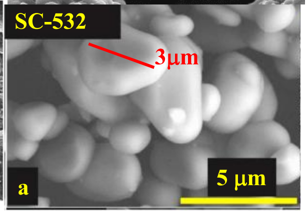






SONY
20 µm





Any proposed future work is subject to change based on funding levels

KEYSTONE 1 SUMMARY

- **New electrolyte developed**
  - Localized high concentration ether-based
    - Forms stable SEI on lithium
    - Over 300 cycles with 811 NMC at coulombic efficiencies over 99.5%
- **Potential source of 1st cycle loss in NMC identified**
  - Rapid fall-off of D_{Li} with increasing Li content
  - At 45° C most of loss eliminated
    - Suggests appropriate doping might ameliorate
- **Coatings on and/or substitution in NMC can be positive**
  - Nb coating/substitution reduces 1st cycle loss
  - Coatings can enhance rate capability
  - Coating can reduce impact of environmental damage to surface
- **NMCs with ≥90% Ni were synthesized**
  - Initial electrochemical tests very promising when PANI added to electrodes
    - 1000 cycles at 99.5% coulombic efficiency

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Technical Back-Up Slides

TECHNICAL BACK-UP SLIDES

None