2016 DOE/OE Peer Review
Washington DC

Recent Progress in Intermediate Temperature Na-Metal Halide Batteries

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Acknowledgement

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Participants

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South Korea

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Outline

- Introduction
- Project Progress
  - Polymer sealing technologies (√)
  - Large cell tests (√)
  - Cathode formula with lower Ni/NaCl ratio (√)
  - Different cathode loadings (√)
  - Simultaneous sintering and conversion of β″-alumina (√)
- Summary (FY16) and Future Plans (FY 17)

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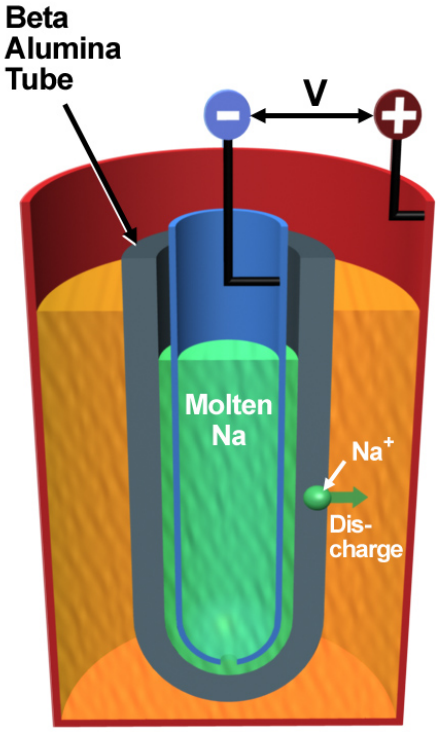
Sodium β″-Alumina Batteries (NBBs)

- **NBBs consisting of molten sodium anode and β"-alumina solid state electrolyte (BASE)**
  - Use of low cost and abundant sodium
  - High specific energy density and specific power
  - Elevated operation temperature (300~350°C)



- **Sodium-metal halide (Na-MH) battery**
  - 2NaCl + Ni (**discharge**) → 2Na + $NiCl_2$ (charge)
  - E = 2.58 V at 280°C
  - Secondary electrolyte: $NaAlCl_4$ (T_m=157°C)
  - **Merits**
    - Superior cell safety
    - Easy assembly in the discharge state
    - Less corrosive nature of cathode materials

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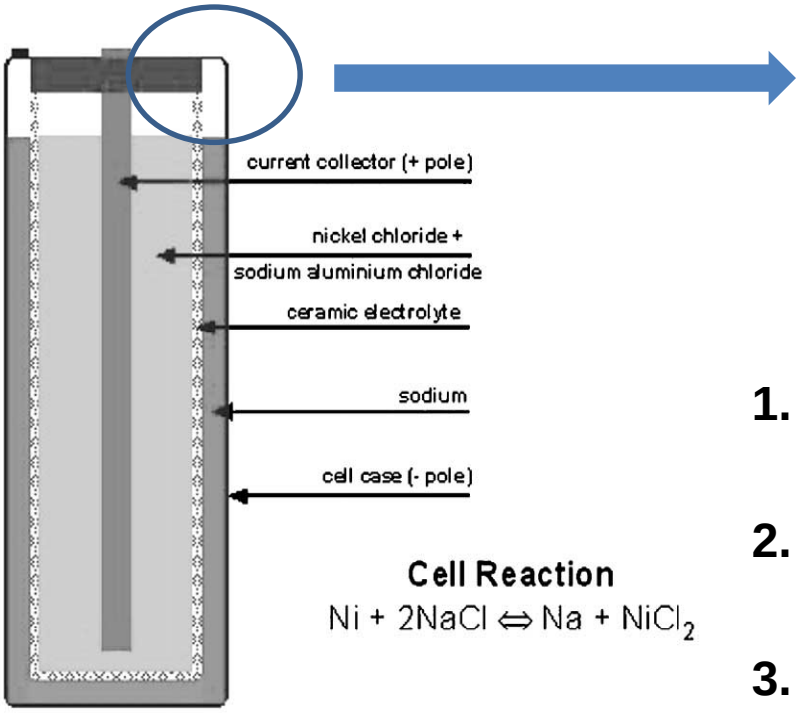
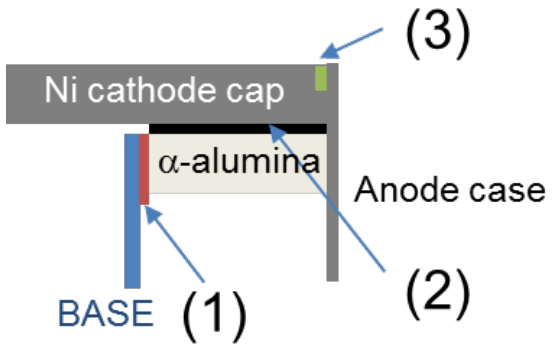
Challenges of Na-MH Batteries

1. High Manufacturing Cost and Complicated Process



Sudworth *J. Power Source*, 100, 149-163 (2001)



1. Glass Sealing:

High purity α-alumina / BASE

2. Thermal Compression Bonding (TCB):

High purity α-alumina / metal

3. Electron Beam Welding

4. Cathode Current Collector:

Long current collector (copper/nickel)

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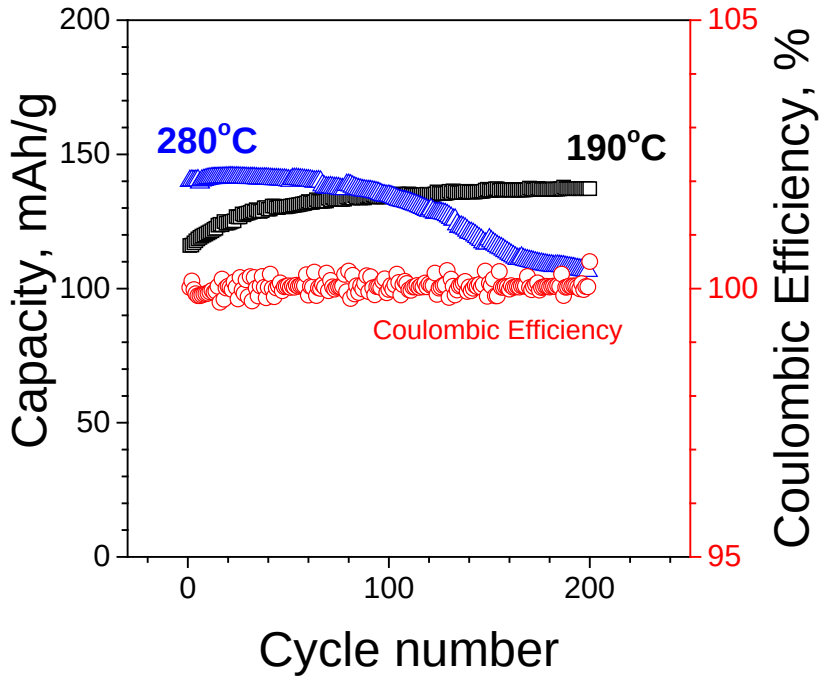
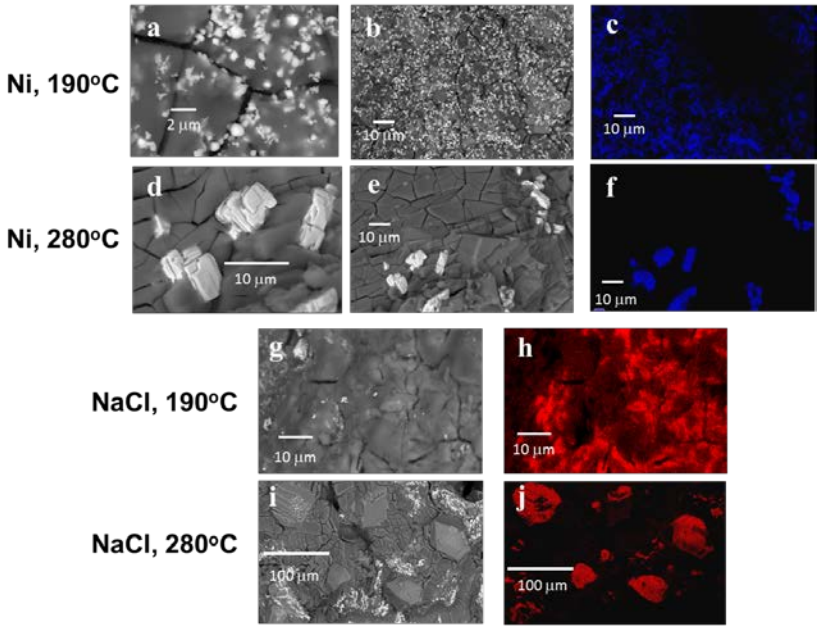
Challenges of Na-MH Batteries

2. Operating Temperature (280°C vs. 190°C)





Li et al. *Nat. Commun.* 7: 10693 (2016).

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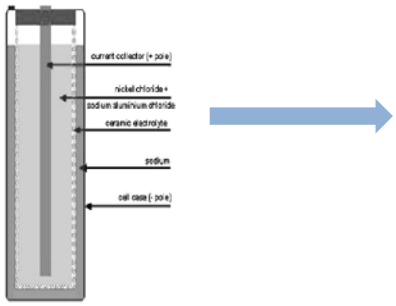
R&D for Na-MH Batteries

❑ Strategies

Develop intermediate temperature (IT, <200°C) chemistries and cell architecture that enable lower materials cost and manufacturing cost.

Tubular type



Planar type

	Tubular (Conventional)	IT Planar
Energy capacity	√	√
Power		√
β" Solid Electrolyte (BASE)	High cost	Low cost
Temperature	≥300˚C	≤200˚C
Packaging	Difficult	Easy

❑ Accomplishments

- Demonstrated improved durability at lower operating temperature
- Enabling use of polymer seals

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Project Goals (Year #1)

- ❑ Developing compliant polymer sealing technologies(√)
- ❑ Design cell architectures for 190°C (√)

	Year #1	Year #2	Year #3
Energy Capacity, Wh	5	10	15
Energy Efficiency, %	-	70	80

- ❑ Technology transfer to RIST (√)
- ❑ Quarterly workshops, teleconferences, KETEP annual review meeting (√)

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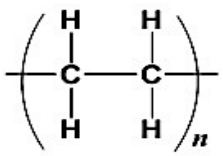
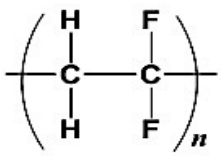
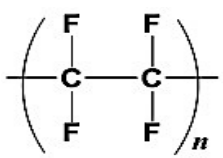
Pre-screening for Polymers



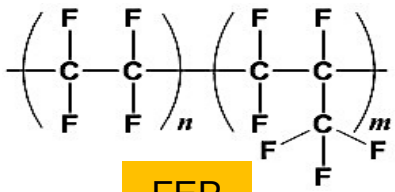
PE



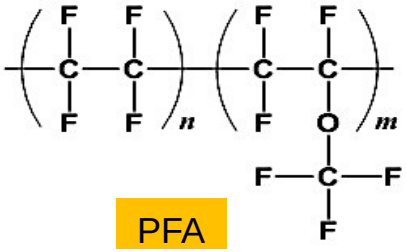
PVDF



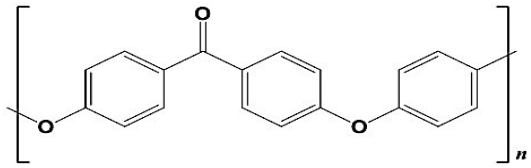
PTFE



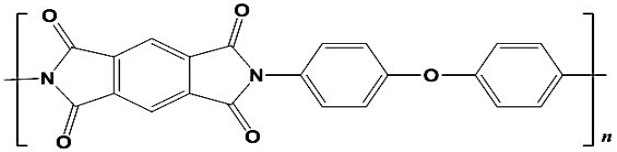
FEP



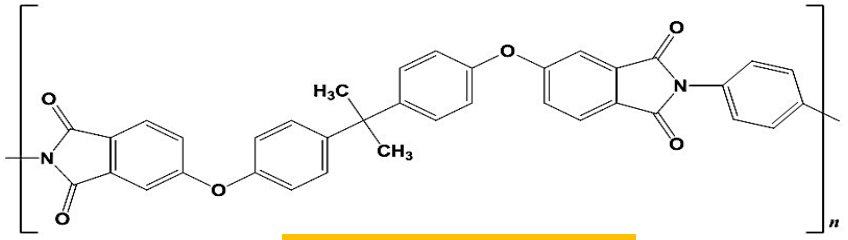
PFA



PEEK



KAPTON



ULTEM (PEI)

#	Polymer	IUPAC name	Chemical formula	T_m
1	PE	Polyethylene	$(C_2H_4)_n$	115–135 °C
2	PVDF	Polyvinylidene fluoride	$(C_2H_2F_2)_n$	177 °C
3	PTFE	Polytetrafluoroethylene	$(C_2F_4)_n$	326.8 °C
4	FEP	Fluorinated ethylene propylene	$(C_2F_4)_n$-$(C_2F_3CF_3)_m$	260 °C
5	PFA	Perfluoroalkoxy alkane	$(C_2F_4)_n$-$(C_2F_3OR')_m$	315 °C
6	PEEK	Polyether ether ketone	$(C_{19}H_{12}O_3)_n$	343 °C
7	Kapton Polyimide	Polyimide	$(C_{22}H_{10}N_2O_5)_n$	> 232 °C
8	Ultem (PEI)	Amorphous thermoplastic polyetherimide	$(C_{37}H_{24}O_6N_2)_n$	204-232 °C

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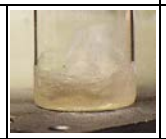
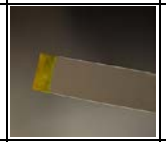
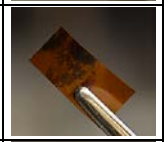
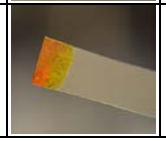
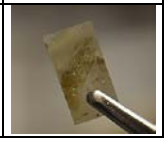
Compatibility with Melts & Molten Na

#	Polymer	$NaAlCl_4$		Na	
1	PE	√		√	
2	PVDF	X		√	
3	PTFE	√		X	
4	FEP	√		X	
5	PFA	√		X	
6	PEEK	X		X	
7	Kapton (Polyimide)	X		X	
8	Ultem (PEI)	X		X	

- Suitable candidates for ***Anode***
  1. **PVDF**
  2. **PE**

- Suitable candidates for ***Cathode***
  1. **PTFE**
  2. **FEP**
  3. **PFA**
  4. **PE**

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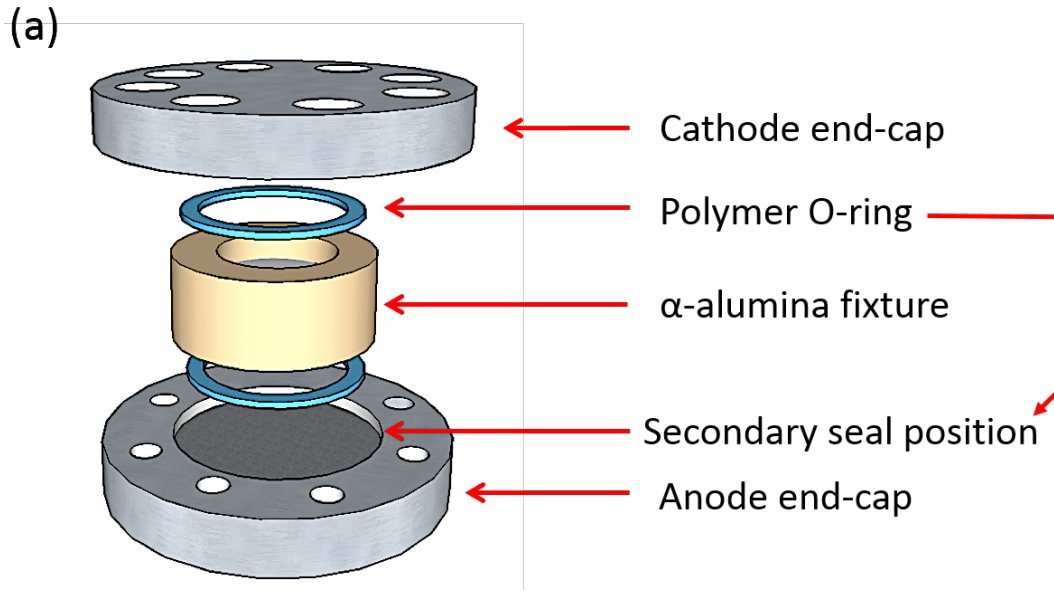
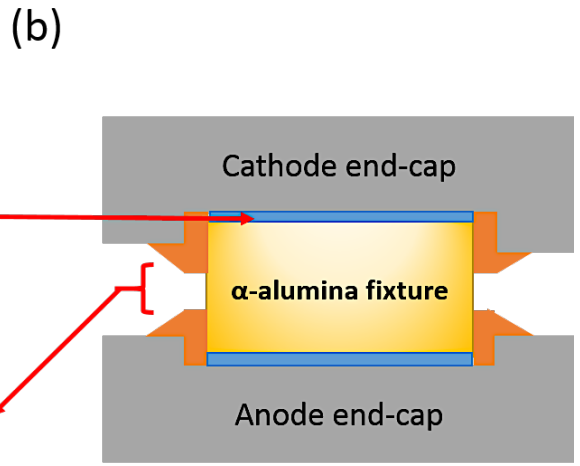
Button Cell Configuration

Button Cell (3cm^2) Test



Single sealing with polymers



Polymer seal with secondary sealing

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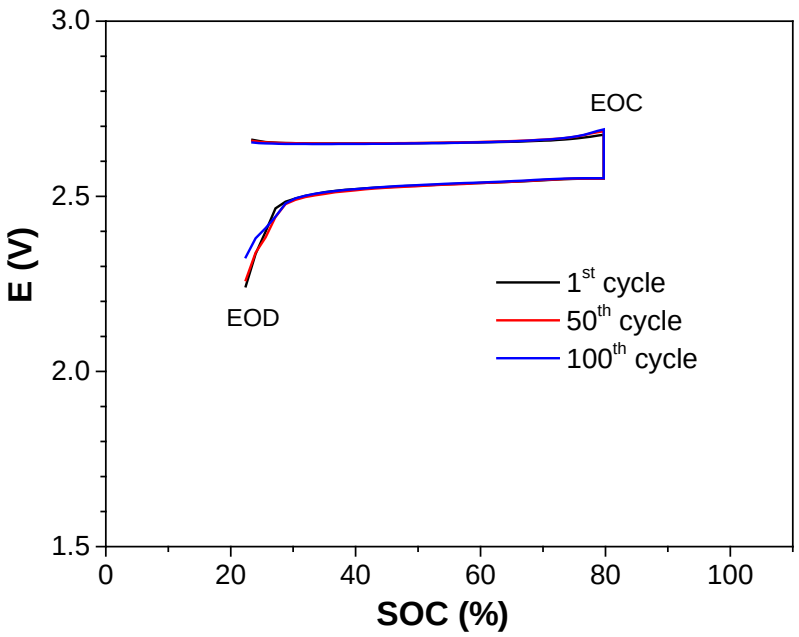
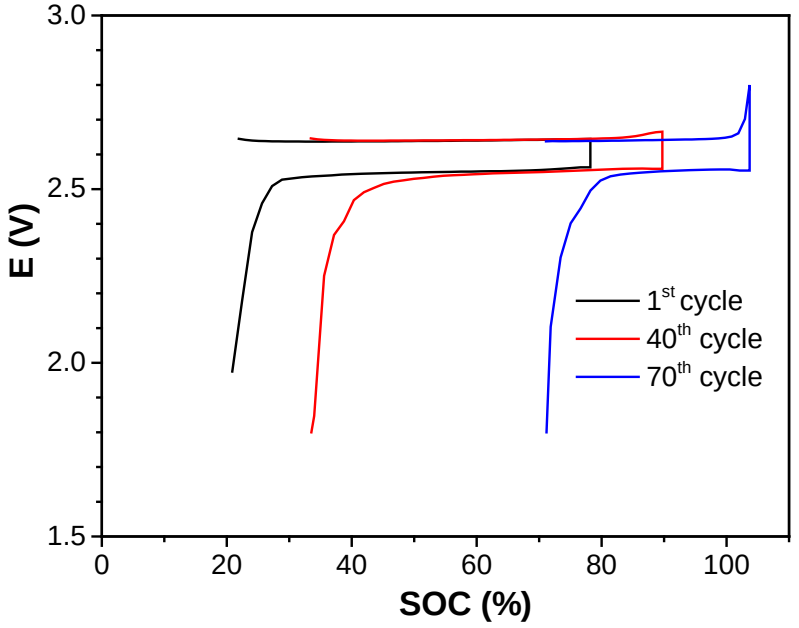
Cell Tests for Polymer Seals on Anode



Successful Case



Failed Case

Cathode sealing: End of Charge Voltage (EOC)
Anode sealing: End of Discharge Voltage (EOD)

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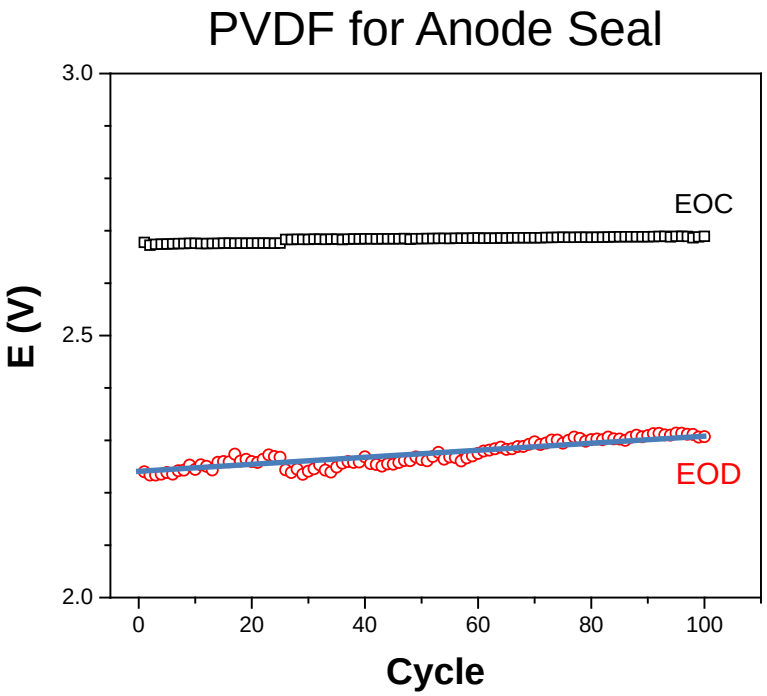
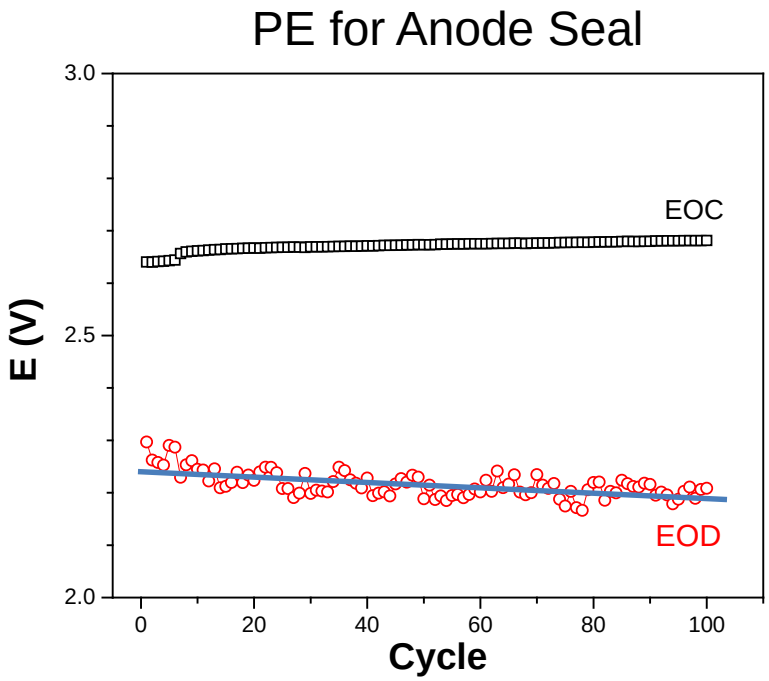
Anode Seal with PVDF & PE





Superior thermal and chemical stability of PVDF vs. PE

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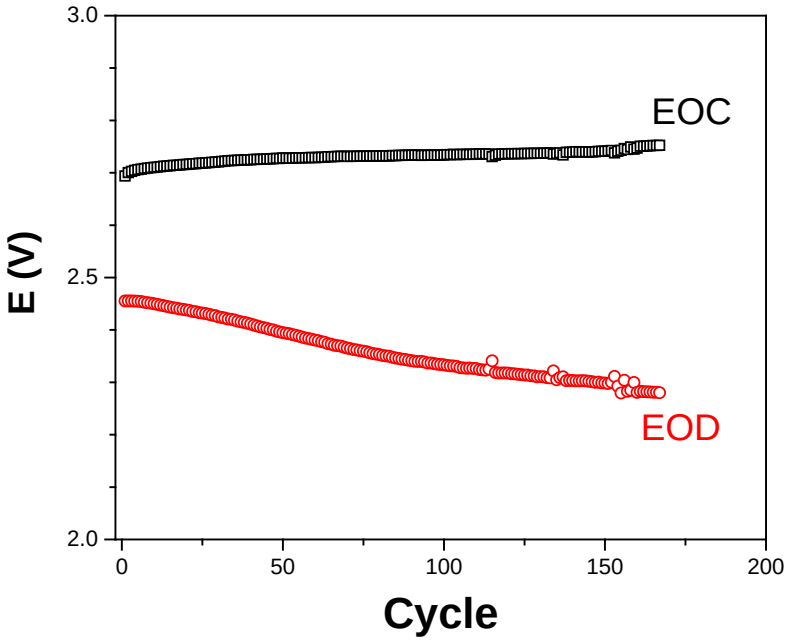
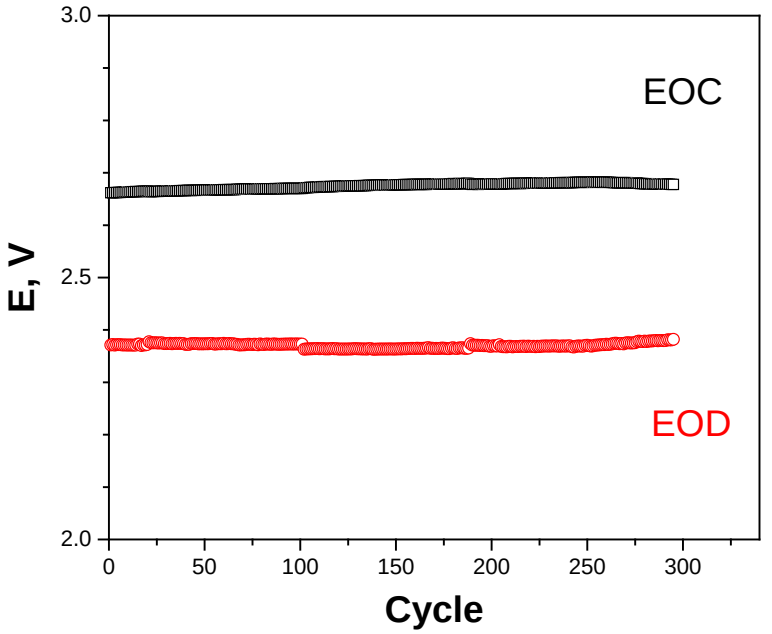
With Secondary Sealants

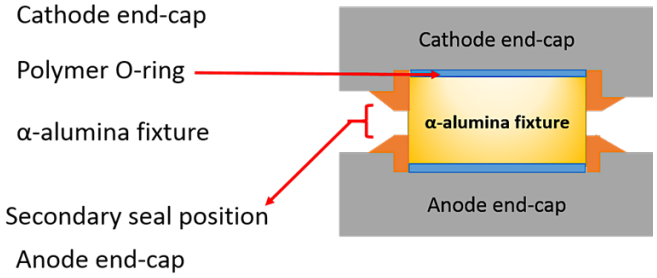
PE Seal on Anode Side

Without Secondary Sealants



With Secondary Sealants





Secondary sealants:
Improve thermal durability of PE

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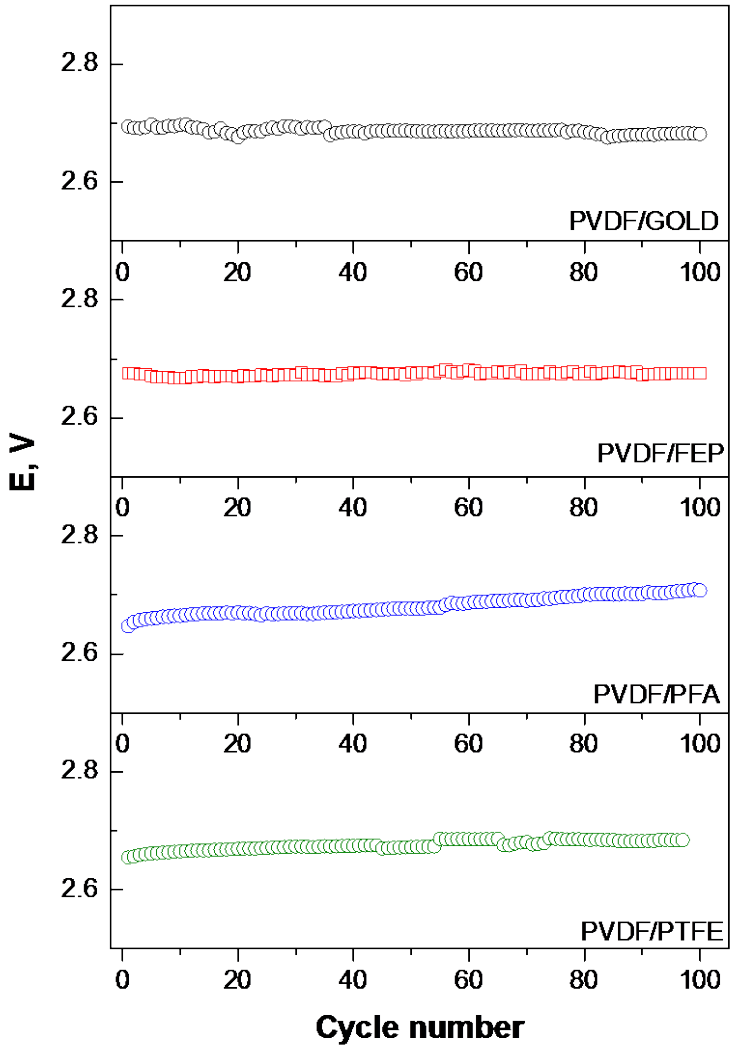
Polymer Compatibility for Cathode



- Three polymers (PFA, FEP, PTFE) show excellent compatibilities and stabilities for cathode materials.

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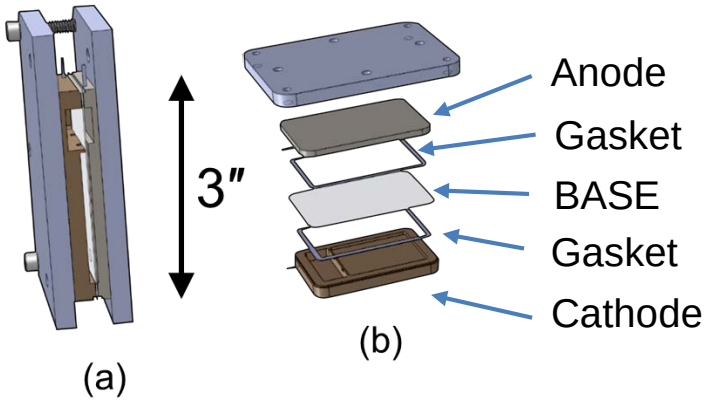
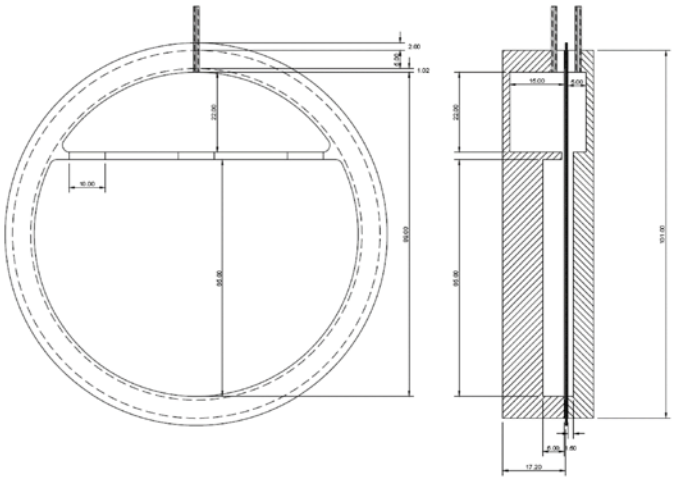
Large Cell Plans

Large IT Na-MH battery





L105 Cell

	I-32 (PNNL)	L105 (PNNL &RIST)	L105 (PNNL &RIST)
BASE area, cm^2	32	50	50
BASE type	PNNL	PNNL	Ionotec
Cathode Loading	1x	2x	3x
Capacity, Ah	~2	~5	~8
Energy, Wh	5	10	15
Milestone	Year #1	Year #2	Year #3

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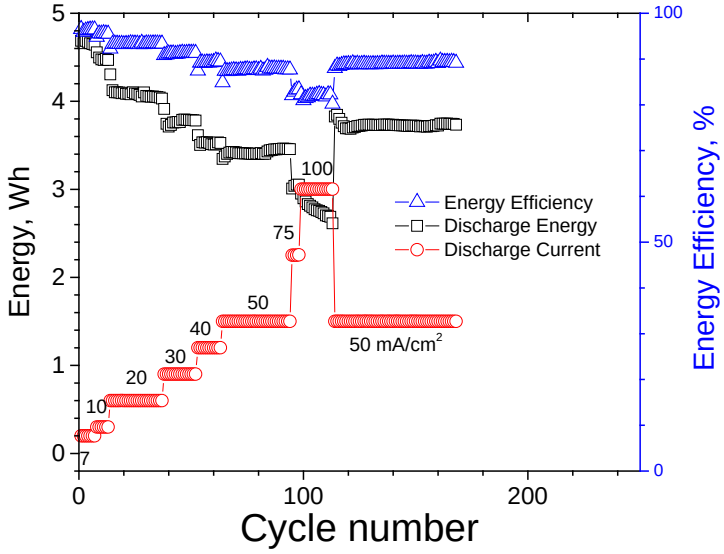
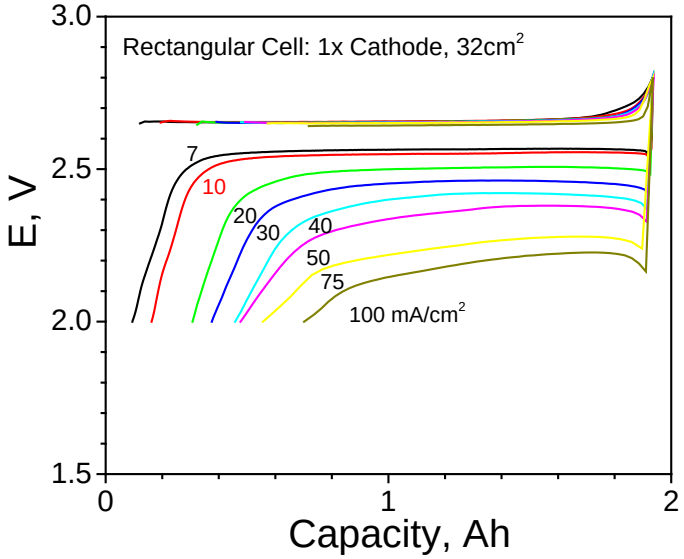
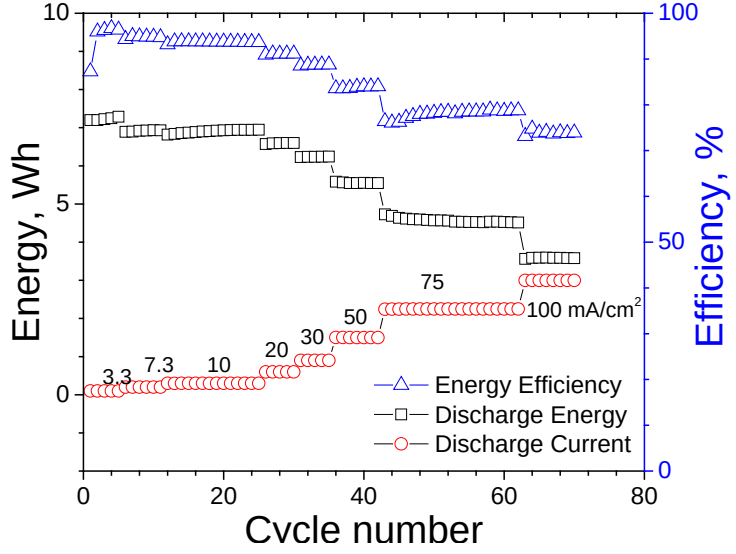
Large Cell Tests

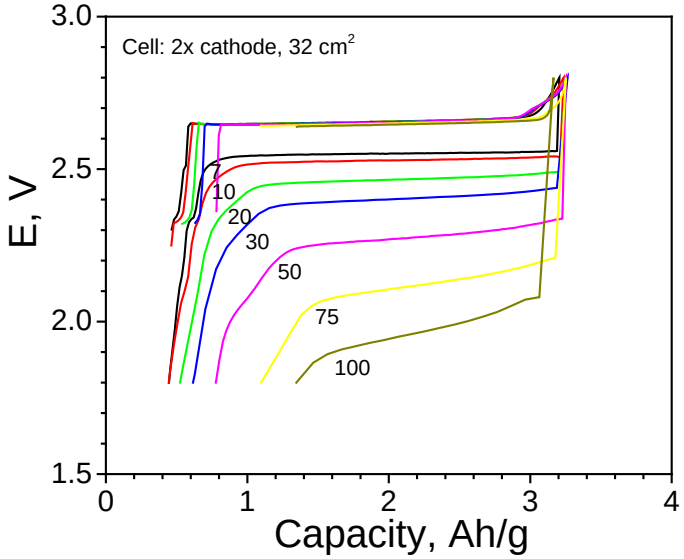
PNNL-I32, 1x Cathode Loading





PNNL-I32, 2x Cathode Loading





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Milestones, Outcomes, and Future Plans

FY 16:

- ❑ 5 Wh cell (**Year #1** milestone)
- ❑ Develop anode seals (PVDF, PE) and cathode seal (FEP, PFA, PTFE)
- ❑ Technology transfer to RIST
- ❑ Papers:
  1) "Advanced Intermediate Temperature Sodium-Nickel Chloride Batteries with Ultra-High Energy Density" ***Nat. Commun.*** 7, 10683 (2016).
  2) "Enhanced Sintering of β″-Al_2O_3/YSZ with the Sintering Aids of TiO_2 and MnO_2", ***J. Power Sources***, 295, 167 (2015).
- ❑ IPs:
  1) "Metallization Pattern on Sold Electrolyte or Porous Support of Sodium Battery Process", US, 9.356,314 (**granted**)
  2) "Hybrid Energy Storage Devices Having Sodium", US, 9,252,461 (**granted**)
  3) "Sodium Beta Energy Storage Devices Comprising Compliant Polymer Seals and a Method for Making and Sealing" (**Aug. 2016, filed**)

FY 17:

- ❑ High Cathode Loadings (Manuscript in preparation)
- ❑ Sealing Technologies (Manuscript in preparation)
- ❑ Cathode Formula (Manuscript in preparation)
- ❑ Large Cells:
  - o 10 Wh cell
  - o Optimizing cell performances

Thank You!

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