Intermediate Temperature Planar Na-Metal Halide Batteries

2012 DOE EES Program Peer Review & Update Meeting
Sept. 26~28, 2012
Washington DC

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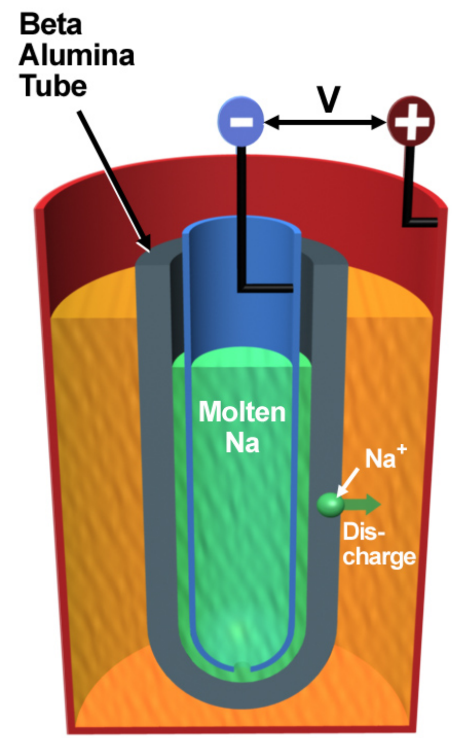
Sponsored by DOE EES Program (Program Manager: Dr. Imre Gyuk)

Sodium β"-Alumina Batteries (NBBs)

- **Batteries consisting of *molten sodium anode* and *β"-Al_2O_3 solid electrolyte* (BASE).**

  - Use of low-cost, abundant sodium → low cost
  - High specific energy density (120~240 Wh/kg)
  - Good specific power (150-230 W/kg)
  - Good candidate as a large-scale energy storage device for renewable energy
  - Operated at relatively high temperature (300~350°C)



Na-S Battery vs. Na-Metal Halide Battery

- **Sodium-sulfur (Na-S) battery**
  - **$2Na + xS \rightarrow Na_2S_x$** (x = 5~3)
    - E = 2.08~1.78 V at 350°C

- **Sodium-nickel chloride (Zebra) battery**
  - **$2Na + NiCl_2 \rightarrow 2NaCl + Ni$**
    - E = 2.58V at 300°C
    - Use of catholyte ($NaAlCl_4$)
  - **Merits**
    - Safe cell failure mode
    - Easiness of assembly in discharged state
    - Less corrosive nature of cathode materials
  - **Drawback**
    - Relatively expensive ➔ **Cost reduction** is a key issue to commercialize this technology for large energy storage applications.

Approaches to Reduce Cost

- **Intermediate Temperature (≤200°C) Na-$NiCl_2$ Battery**
  - Use of economical construction materials and process such as polymer seals, enabling high throughput manufacturing methods
  - Low maintenance cost
  - Better cycle life by suppressing degradation mechanisms
- **Zn-Based Battery**
  - Replacement of nickel with low-cost zinc

Intermediate Temperature Na-$NiCl_2$ Battery

Technical Challenges

- **High cell polarizations at reduced temperatures**
  - Thick BASE tube (1~2 mm thick)
    - Use of thin high-strength composite planar BASE
  - *Catholyte $NaAlCl_4$ (T_m = 157 °C)*
- ***Wettability of Na melt on BASE at reduced temperatures***

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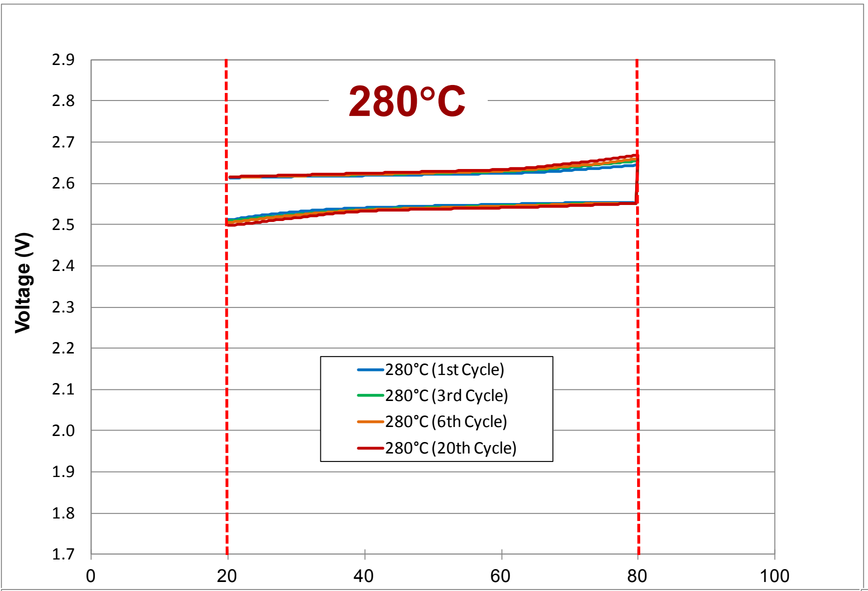
Na-NiCl$_2$ Battery with Thin Planar BASE

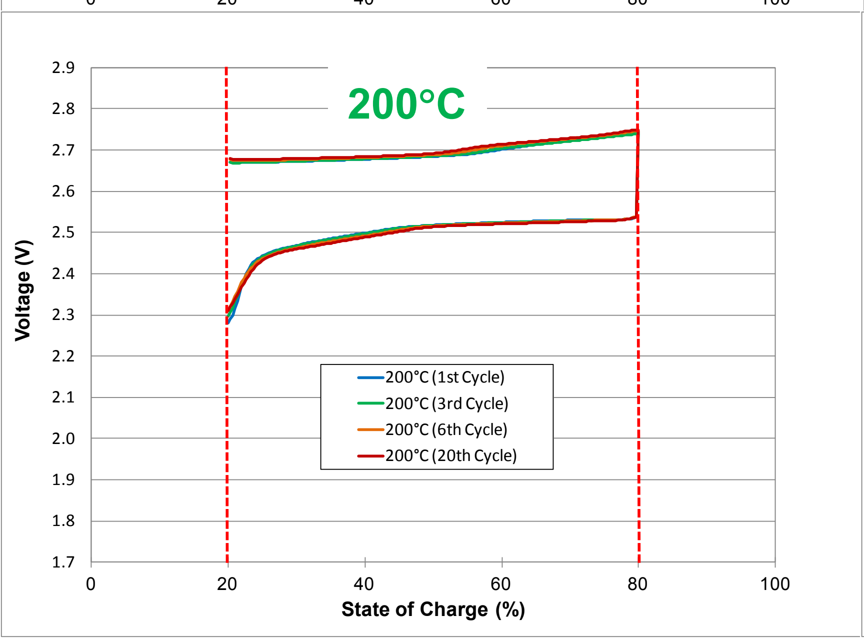
- **V vs. SoC cycled at various temperatures under C/3 rate**

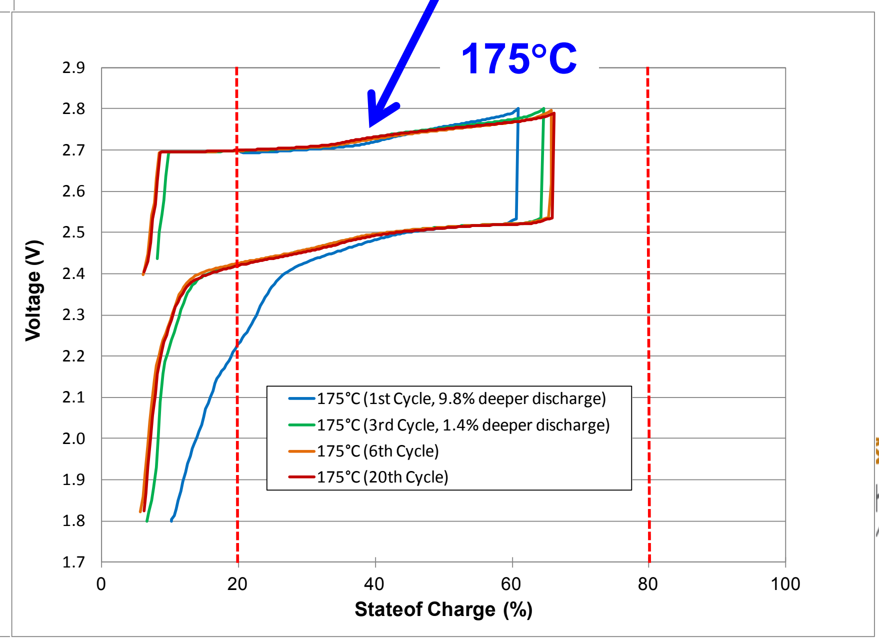


Test conditions

- 3 cm^2 active area button cell
- 1.5 g cathode (Ni, NaCl, $NaAlCl_4$)
- 60% Theoretical capacity (20-80% SoC)
- 150 Whr/kg @ C/3

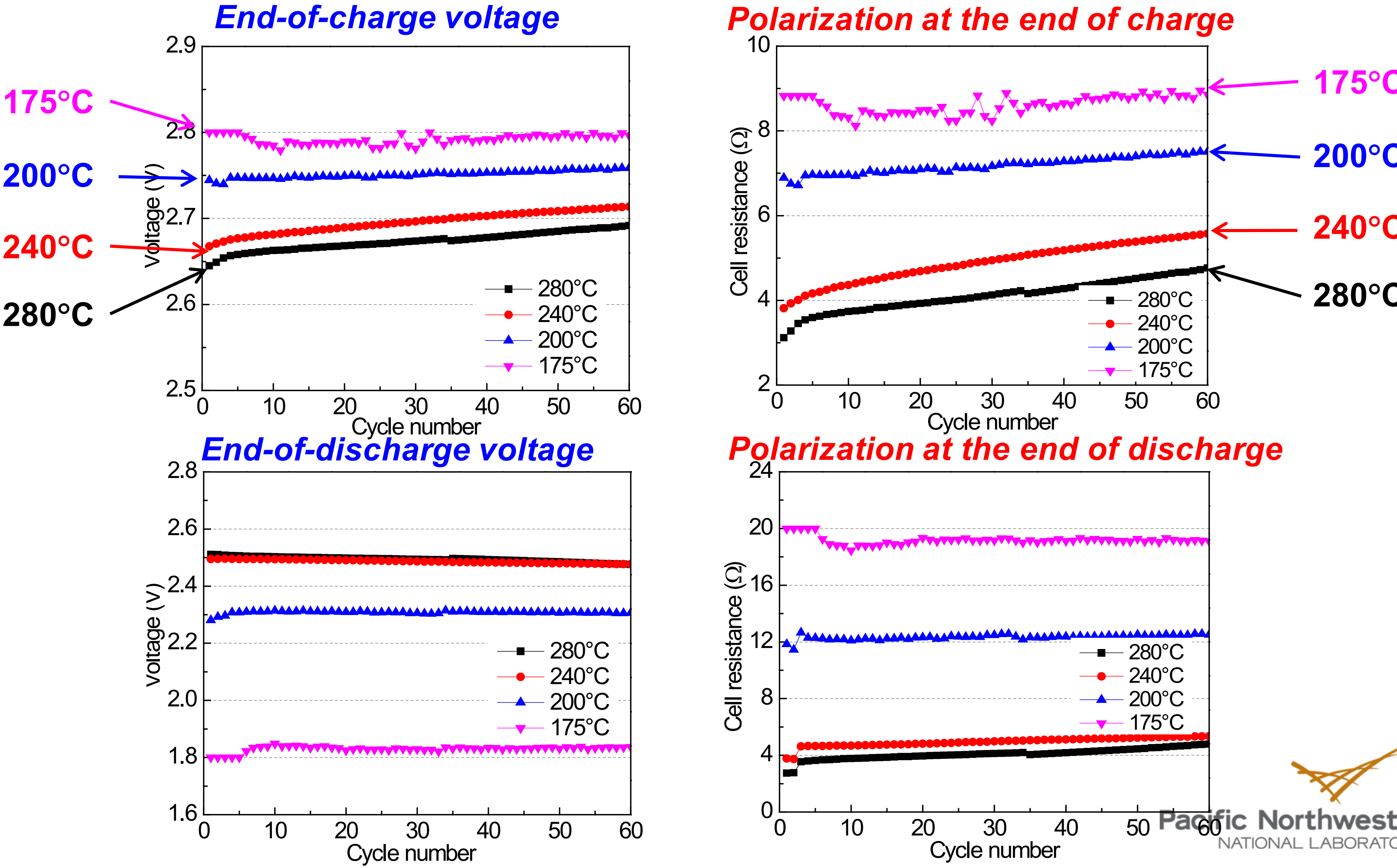
Cannot charge fully at 175^{o}C, gradually shift to more discharged state





Na-NiCl$_2$ Battery with Thin Planar BASE

- **Cell voltage and corresponding resistance at various temperatures**



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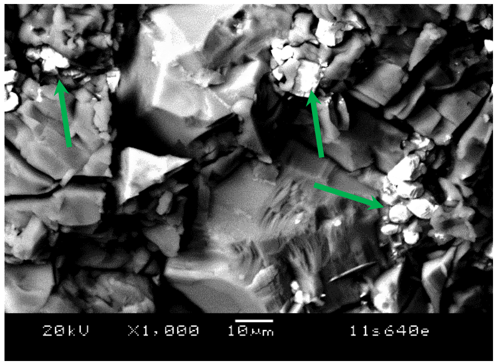
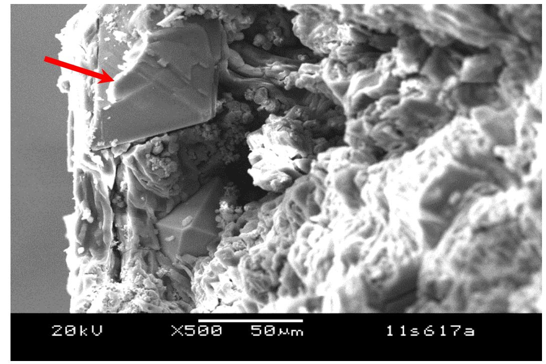
Na-NiCl$_2$ Battery with Thin Planar BASE

- **Backscattered electron images of the cathodes after 60 cycles**

Ni particle | **NaCl particles**

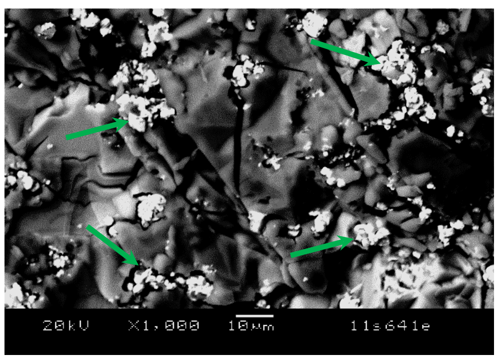
280°C

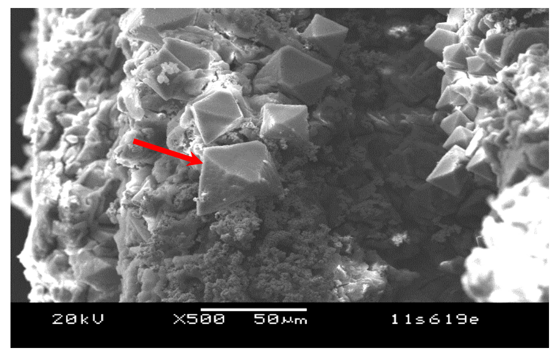




NaCl ~ 50µm

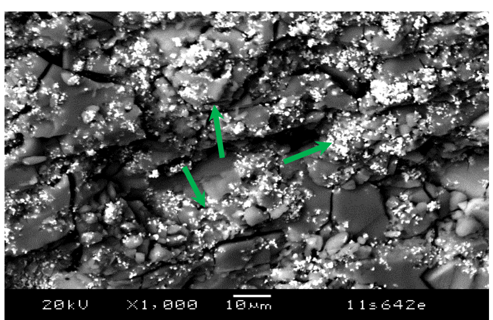
240°C





NaCl ~ 25µm

175°C

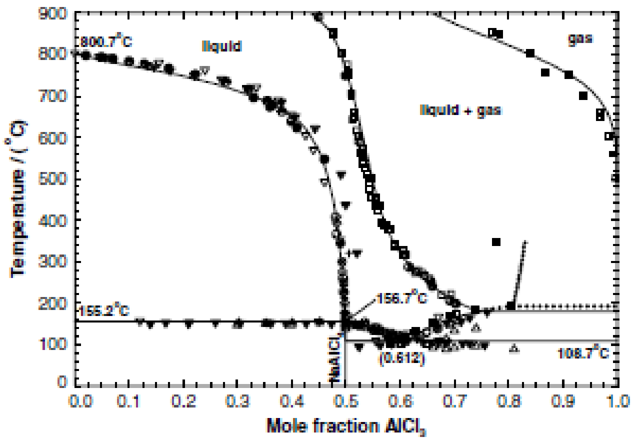


Starting NaCl size ~ 10 µm, no growth observed after cycling at 175°C

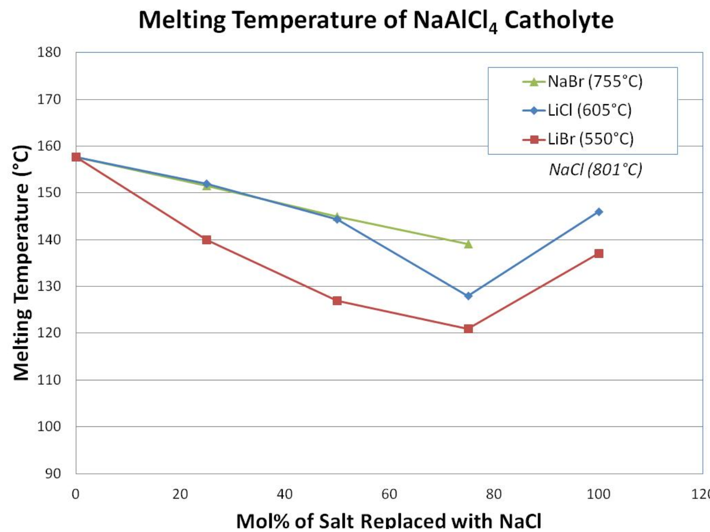
Low T_m Catholyte Development

▶ Replacement of NaCl with lower melting-point salts

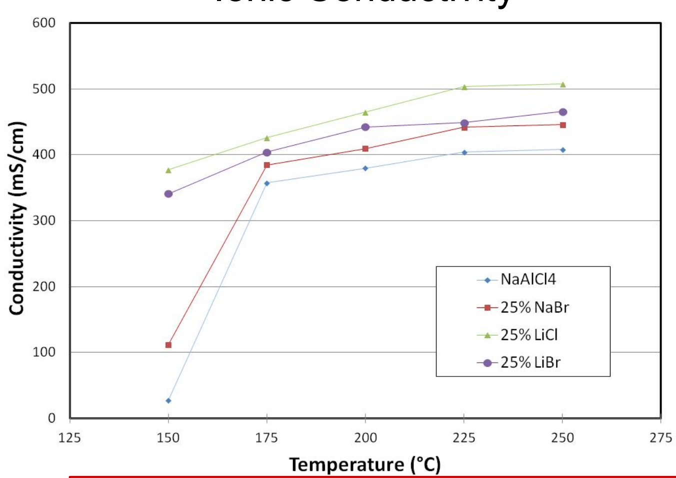
$NaAlCl_4$ (T_m=157°C)



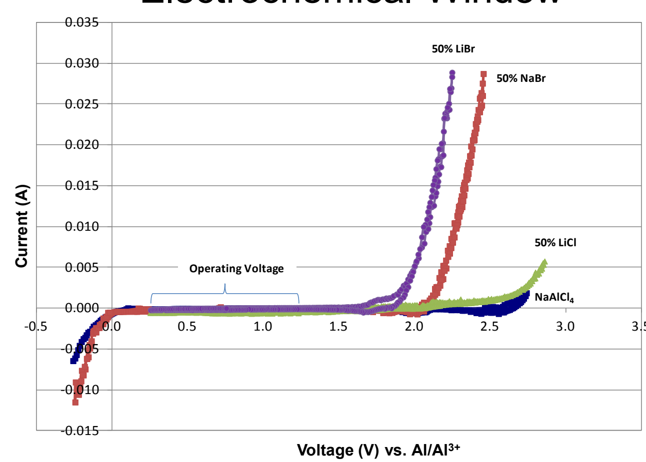
Robelin et. al, J. Chem. Thermodynamics (2004)



Ionic Conductivity



Electrochemical Window



- Decrease T_m of catholyte by 20 - 40°C
- High ionic conductivity < 200°C with ≥ 25% salt replacement.
- Does not impact electrochemical stability of catholyte.

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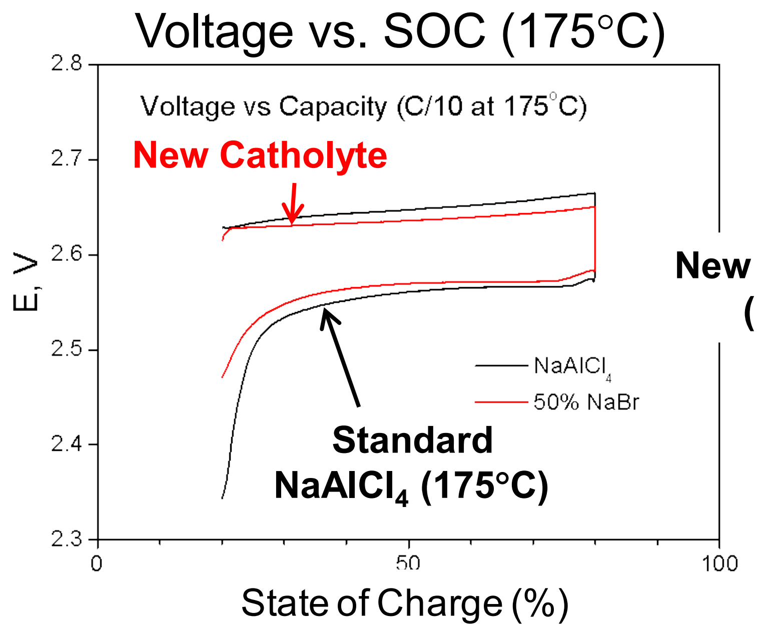
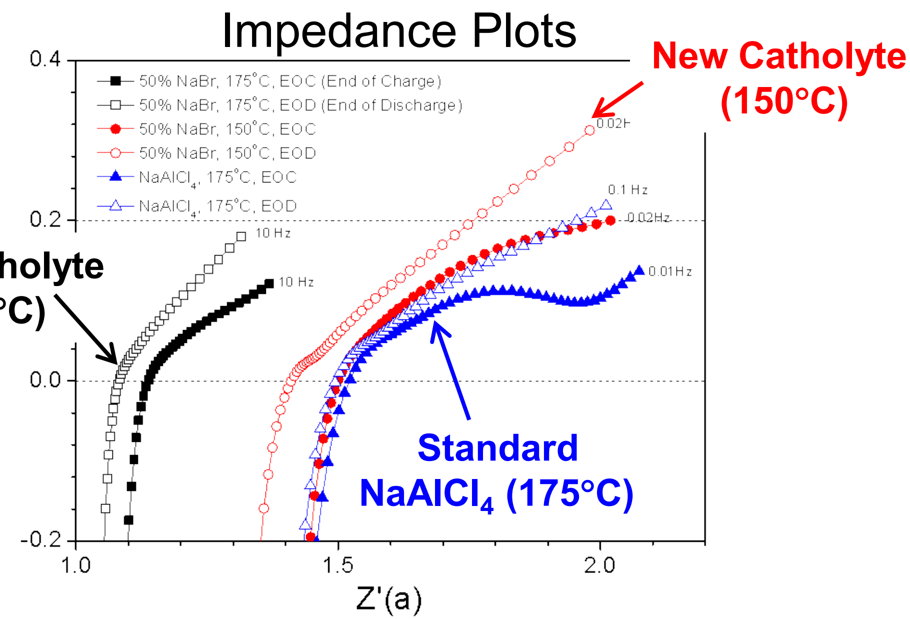
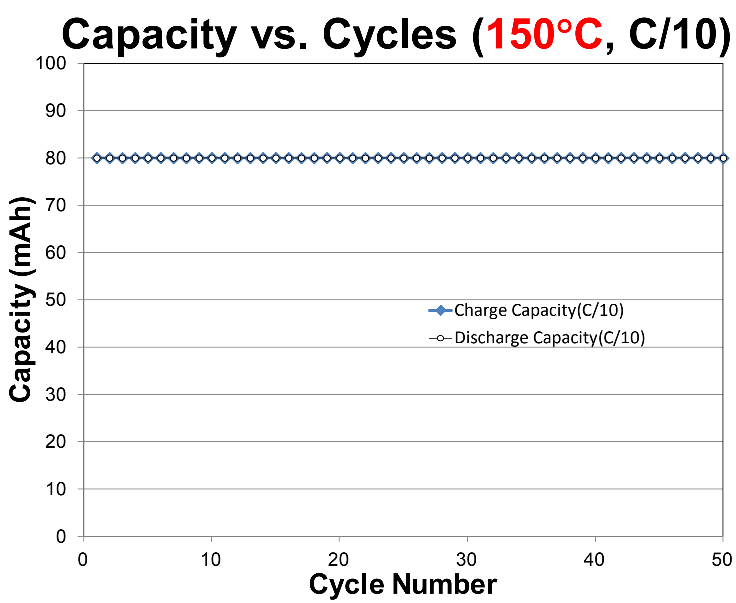
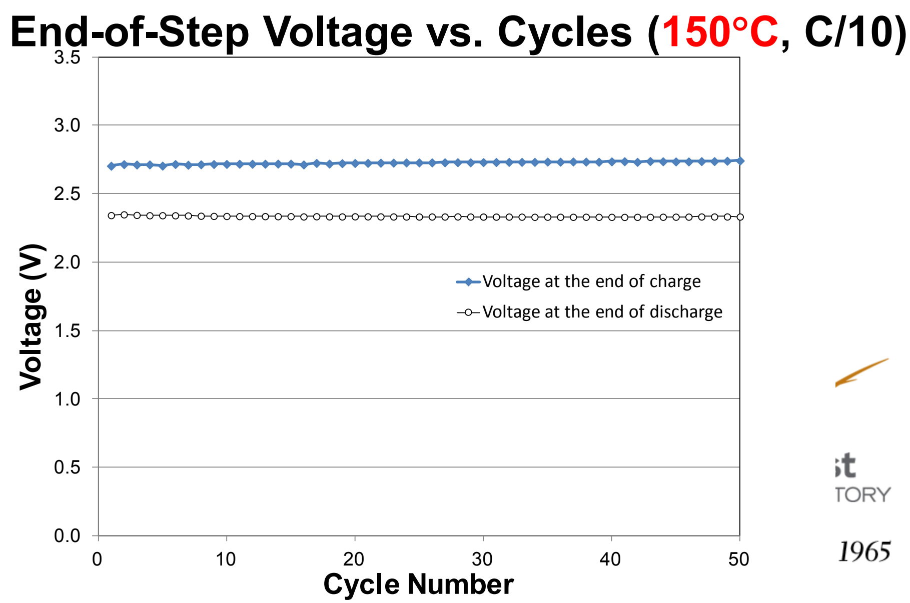
Low T_m Catholyte Development

- **Electrochemical Performance (50% NaCl replacement w/ NaBr)**





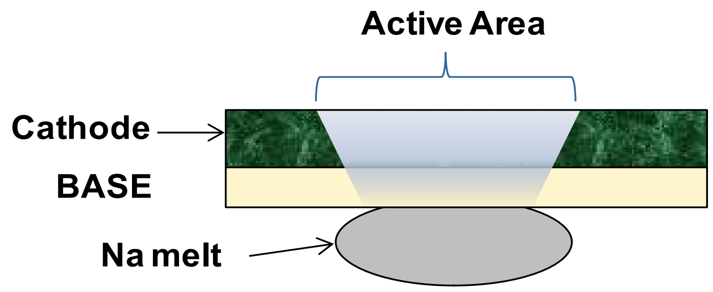


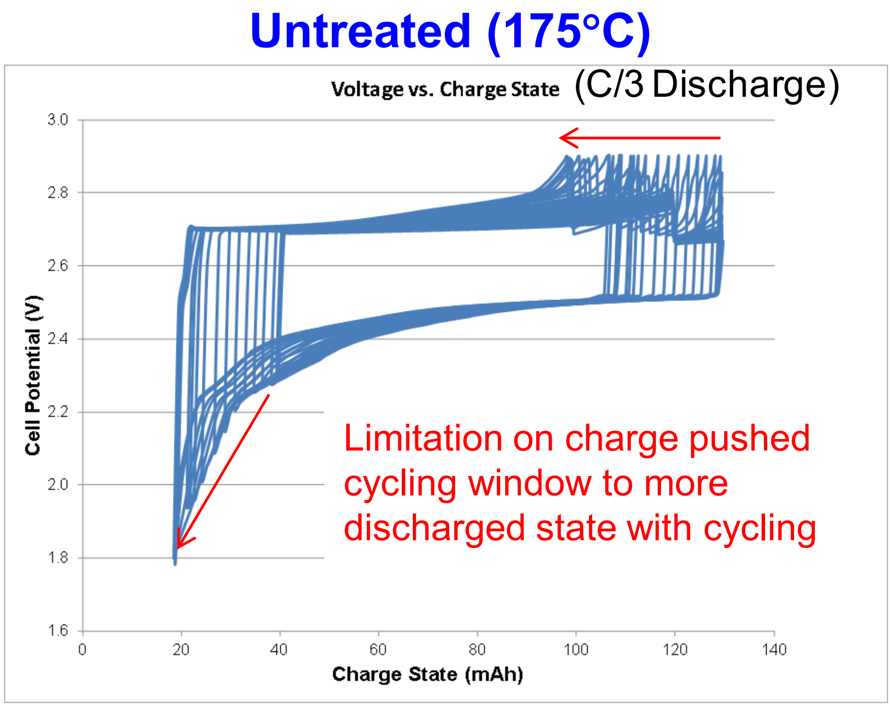


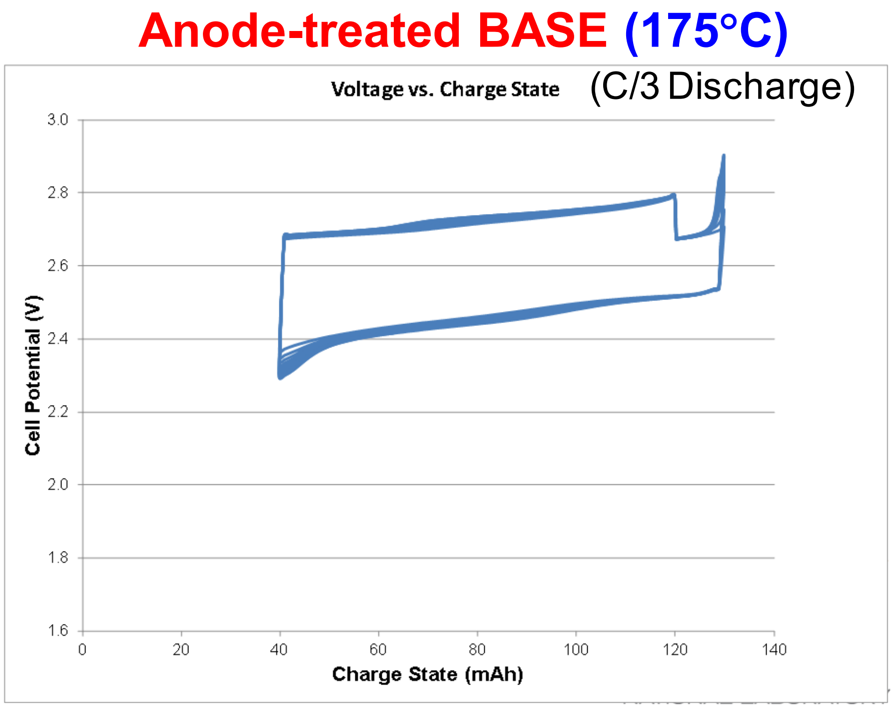
1965

Low Temperature Na Wetting

BASE Treatment on Anode Side







Na-$ZnCl_2$ Battery

▶ Parthasarathy et al. *

- Na-$ZnCl_2$ battery with ***$ZnCl_2$-NaCl* catholyte**
- Operate at high temperature (≥350°C) due to high eutectic point of $ZnCl_2$-NaCl catholyte (Tm=253°C)
- ≥ 33 mol% $ZnCl_2$ cannot be discharged to maintain the molten state of $ZnCl_2$-NaCl catholyte
- Use of eutectic $ZnCl_2$-NaCl catholyte makes the cell assembly in partially charged state (use of sodium in anode)

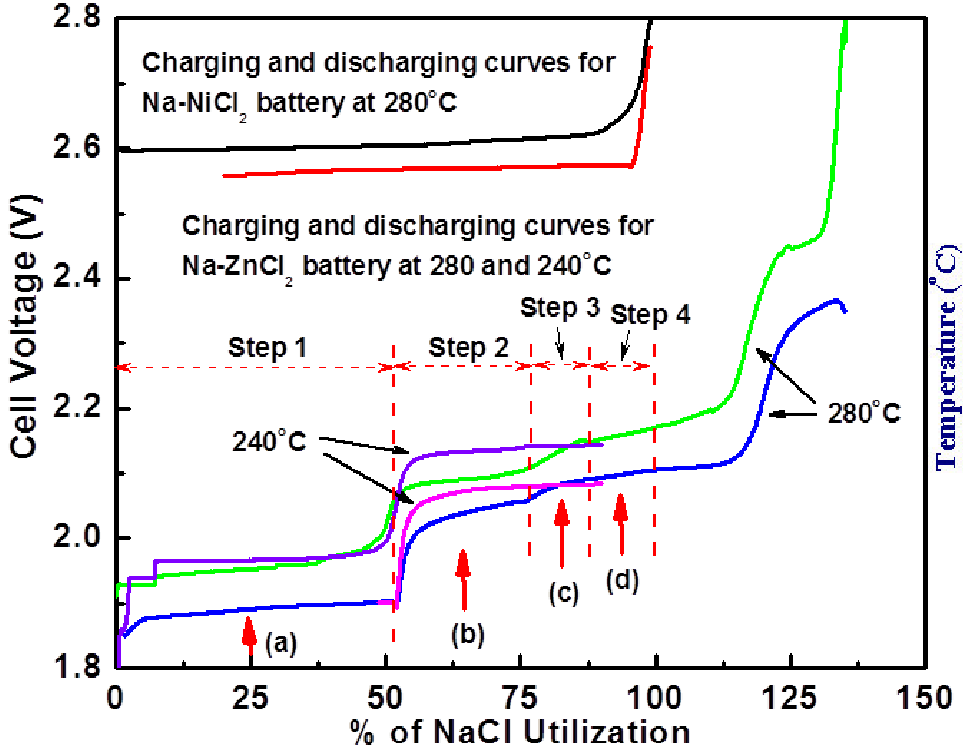
▶ New Na-$ZnCl_2$ Battery

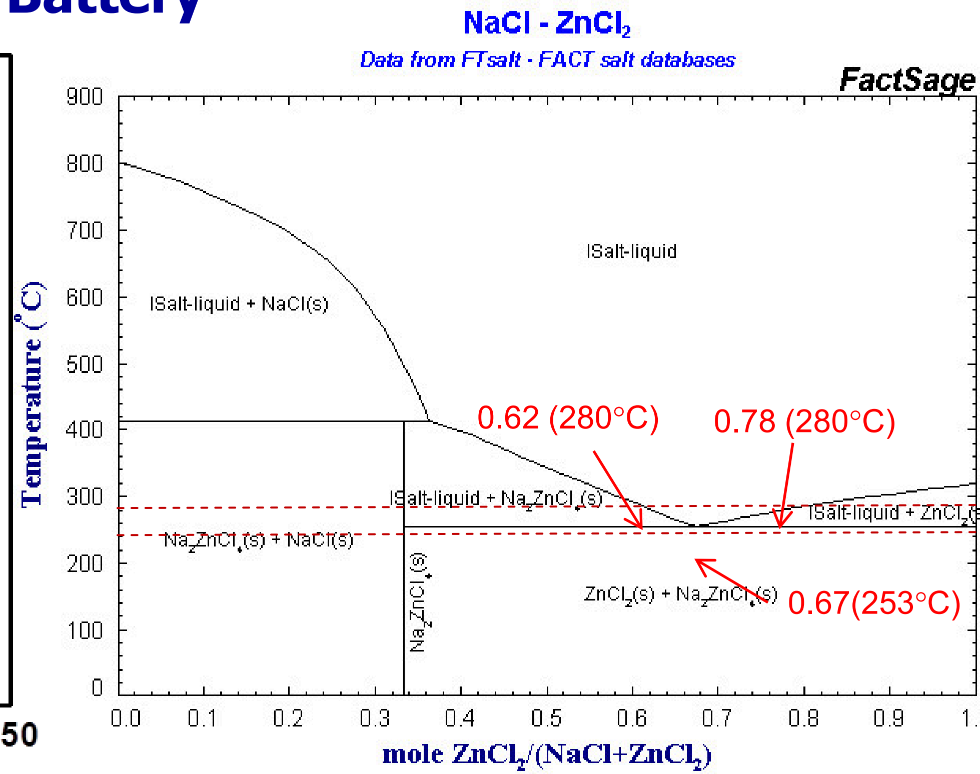
- Cathode consists of active materials (NaCl + Zn), $NaAlCl_4$ catholyte, and electrically conducting materials (metals, carbon, etc) in the form of powder, foam, mesh, etc.
- Assembled in discharged state (no addition of sodium in anode)
- Can be operated at relatively lower temperature (<300°C)
- Can fully utilize $ZnCl_2$ during discharge

* *P. Parthasarathy, N. Weber, A.V. Virkar, ECS Trans. 6 (2007) 67*

Na-$ZnCl_2$ Battery

▶ **Na-$ZnCl_2$ Battery vs. Na-$NiCl_2$ Battery**





280°C (liquid phase formation)

1. $4NaCl + Zn \Leftrightarrow Na_2ZnCl_4 + 2Na$ — E ~ 1.92 V
2. $Na_2ZnCl_4 + Zn \Leftrightarrow$ **Salt Liquid** ($ZnCl_2$: 62 mol%) + 2Na — E ~ 2.07 V
3. **Liquid** (lower $ZnCl_2$) + Zn $\Leftrightarrow$ **Liquid** (higher $ZnCl_2$) + 2Na — E: 2.07~ 2.12 V
4. **Salt Liquid** ($ZnCl_2$: 78 mol%) + Zn $\Leftrightarrow ZnCl_2 + 2Na$ — E ~ 2.13 V

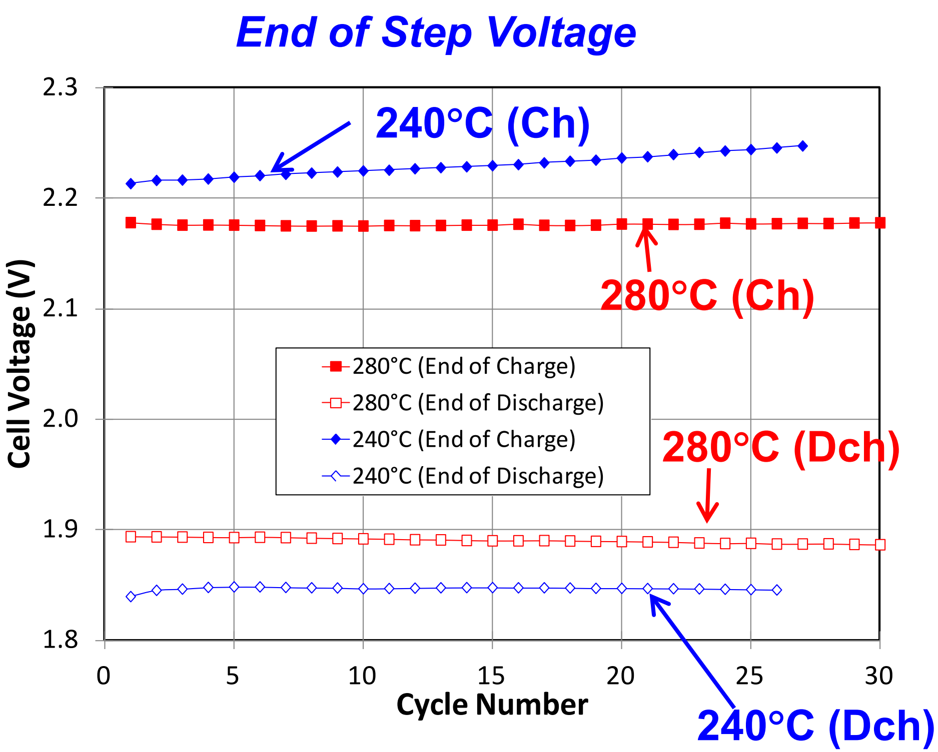
240°C (solid-state reactions)

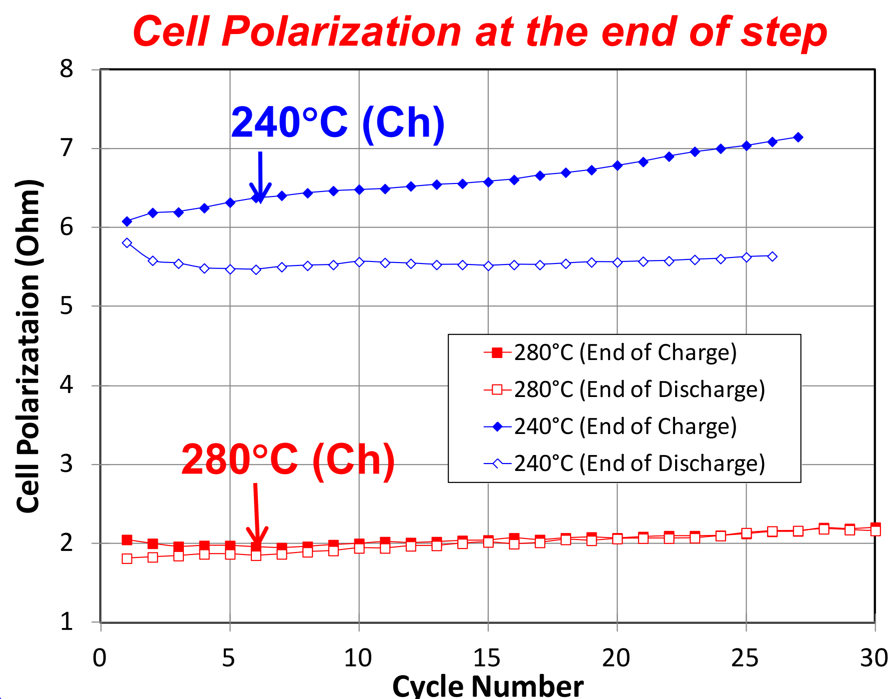
1. $4NaCl + Zn \Leftrightarrow Na_2ZnCl_4 + 2Na$
2. $Na_2ZnCl_4 + Zn \Leftrightarrow ZnCl_2 + 2Na$

Na-$ZnCl_2$ Battery

▶ Cell voltage and corresponding resistance at 280°C and 240°C

- C/3, 45% theoretical capacity





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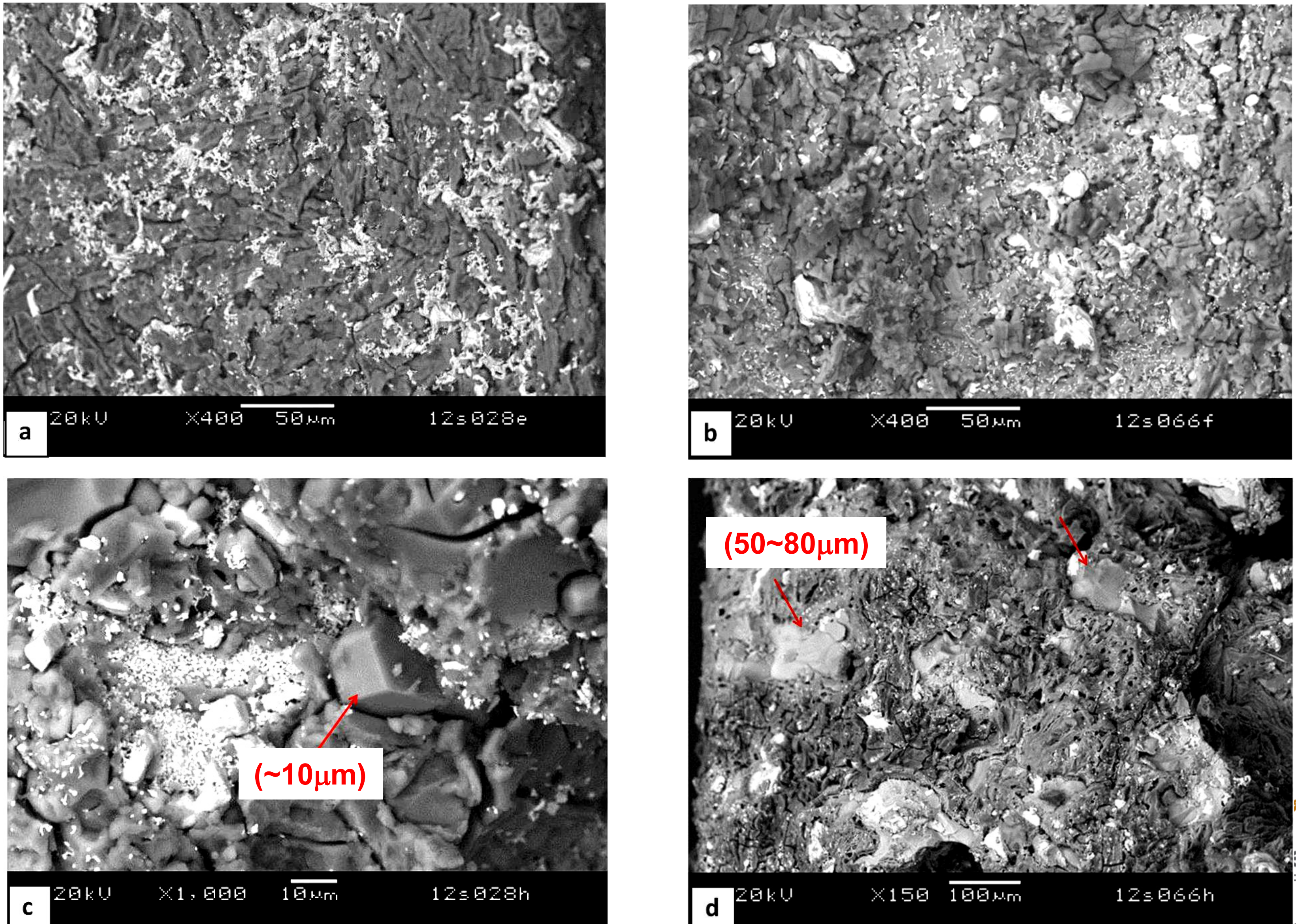
Na-ZnCl$_2$ Battery

280°C | 240°C

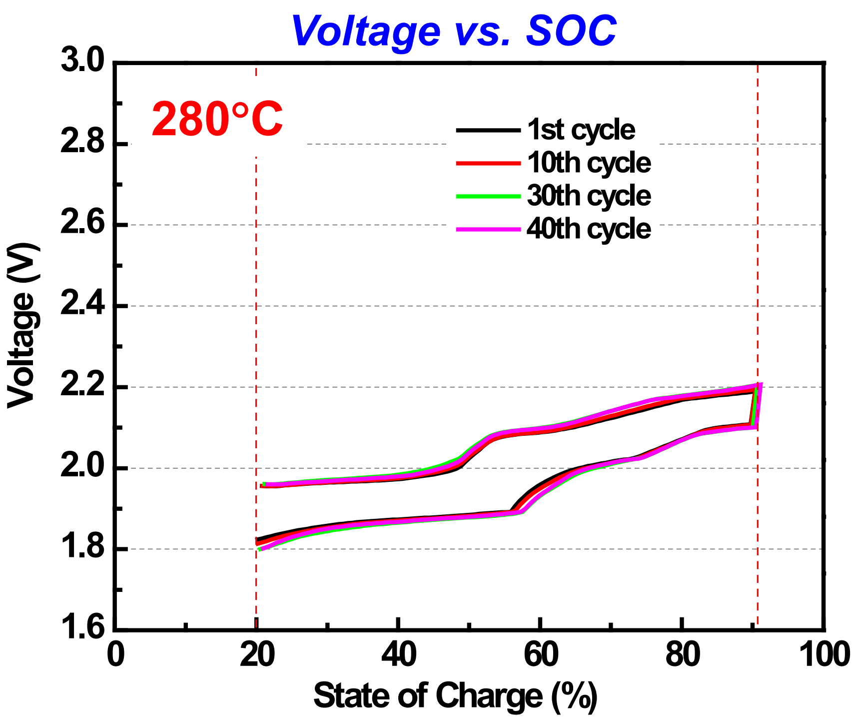
Zn

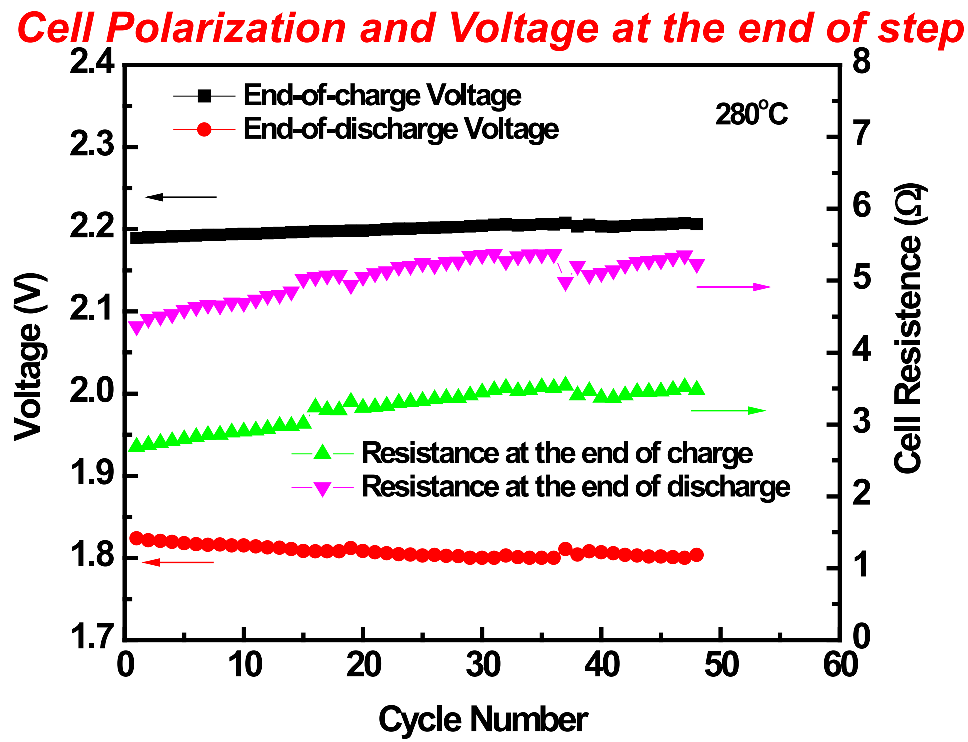
NaCl



Na-$ZnCl_2$ Battery

- Deep cycling (73% Theoretical capacity)





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Summary

Intermediate Temperature Na-$NiCl_2$ Battery

- Intermediate temperature (≤200°C) Na-$NiCl_2$ battery was successfully developed by incorporating thin planar BASE, **low melting temperature catholyte**, and **anode-treated BASE**.
- These cells show much reduced degradation compared to high temperature cells (at 175 with 60% cycling capacity under C/3; at 150°C with 53% cycling capacity under C/10).

New Na-$ZnCl_2$ Battery

- New Na-$ZnCl_2$ battery with $NaAlCl_4$ catholyte was successfully tested at 280°C at which electrochemical reactions include liquid phase formation.
- The formation of the liquid phase helps to decrease degradation possibly due to the suppression of particle growth
- This battery was capable of deep cycling up to >70% of theoretical capacity with good stability.

Future Work

- **Large-scale cell test (64 cm^2 active area)**
- **Long term test**
- Other
  - Polymer seal development
  - Thin BASE ($\leq$50 μm) with porous support
  - Investigation on degradation mechanisms

Publications

- X. Lu, G. Li, J.Y. Kim, J.P. Lemmon, V.L. Sprenkle, Z. Yang, "The Effects of Temperature on the Electrochemical Performance of Sodium-Nickel Chloride Batteries", J. Power Sources 215 (2012) 288
- G. Li, X. Lu, C.A Coyle, J.Y. Kim, J.P. Lemmon, V.L. Sprenkle, Z. Yang, "Novel ternary molten salt electrolytes for intermediate-temperature sodium/nickel chloride batteries," J. Power Sources 220 (2012) 193
- D.M. Reed, G.W. Coffey, E.S. Mast, N.L. Canfield, J. Mansurov, X. Lu, and V.L. Sprenkle, "Thin BASE ($\leq$50 μm) with porous support," J. Power Sources, submitted
- X. Lu, G. Li, J.Y. Kim, J.P. Lemmon, V.L. Sprenkle, Z. Yang, "Novel Sodium-Zinc Chloride Battery," in preparation