Investigating Anodes Based on Calcium Zincate (Ca[Zn(OH)₃]₂·2H₂O) for Improved Cycle Life in Rechargeable Alkaline Zinc Batteries

Patrick K. Yang¹,²,³, Damon E. Turney¹, Michael Nyce³, Timothy N. Lambert⁴, Stephen O’Brien¹,²,³, Sanjoy Banerjee¹,³,⁵,⁶, Gautam G. Yadav⁴, Jinchao Huang⁴, Meir Weiner⁴, Shinju Yang⁶

¹ Ph.D. Program in Chemistry, The Graduate Center of the City University of New York
² Department of Chemistry and Biochemistry, The City College of New York
³ The CUNY Energy Institute, The City College of New York
⁴ Department of Photovoltaics and Materials Technology, Sandia National Laboratories
⁵ Department of Chemical Engineering, The City College of New York
⁶ Urban Electric Power Inc., Pearl River


Objective: Understand the role of various additives on the cycling performance of calcium zincate anodes at high utilization of the zinc.

Background:
- Metallic zinc (Zn) is used industrially for primary and rechargeable Zn batteries such as Zn/Ni, Zn/Air, Ag/Zn, and Zn/MnO₂
- Zinc chemistry provides a high theoretical capacity, relative abundance, non-toxic, and non-flammable nature which make them inherently safer for energy storage
- Failure mechanisms of zinc batteries include passivation, shape change/redistribution, dendrite formation, hydrogen evolution, and the crossover of zincate (Zn(OH)₃)²⁻ into the cathode
- Preliminary results indicate that anodes containing calcium zincate may mitigate some of these problems due to its low solubility in KOH electrolyte
- On charge the reaction product Ca(OH)₂ ready compounds with zincate ions to keep zincate concentrations low in the porous electrode material.

Preliminary Experiments

Cycling Results (Ongoing)

<table>
<thead>
<tr>
<th>Metal wt.%</th>
<th>Zinc Oxide wt.%</th>
<th>Calcium Zincate Rough Estimate (g/kg)</th>
<th>BiO₃ wt.%</th>
<th>PTFE wt.%</th>
<th>Water wt.%</th>
<th>Total wt.</th>
<th>Utilization %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2</td>
<td>3.2</td>
<td>10</td>
<td>3</td>
<td>0.3</td>
<td>19</td>
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Scaled Up Sharma Calcium Zincate Standard RT Recipe

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Rough Estimate on Raw Materials Cost at Scale*

<table>
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<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>Volume Expansion vs. pure Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic Zinc</td>
<td>7.133</td>
<td>1</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>5.61</td>
<td>1.27</td>
</tr>
<tr>
<td>Calcium Zincate</td>
<td>2.59</td>
<td>2.75</td>
</tr>
</tbody>
</table>

Design of Experiments: 2 x 3 in Anode vs SiNi Fabrication

Design of Experiments: Battery Cycling Results (Ongoing)

Design of Experiments: Anode Compositions

Total mass (g) Active material (g) Anode Composition in wt.% Cell # Metal wt.% Zinc wt.% Zincate wt.% 10 wt.% BiO₃ wt.% 4 wt.% PTFE wt.% make of Zn wt.% of Zn Utilization Rough Cost of Anode (g/kg)

9.5 0.03 Zinc/Anode 90% Zn 0 0 0 0.00 0.0 0.36 0.14 9.03 50.00 47.65
10.5 0.03 Baseline 80% Zinc + 10% BiO₃ 0 0 0 1.05 0.42 0.14 9.03 50.00 58.59
12.7 10.92 80% Zn + 20% Ca Zinc + 10% BiO₃ 1 7.62 3.30 1.21 0.48 0.14 9.02 50.00 64.98 (1.1 x Baseline)
17.6 15.14 20% Zn + 80% Calcium Zinc + 10% BiO₃ 3 4.58 10.56 1.67 0.67 0.14 9.05 50.00 79.39 (1.1 x Baseline)
24.8 21.33 80% Zinc + 20% Bismuth Oxide 3 0.00 21.33 2.36 0.94 0.14 9.03 50.00 100.38 (1.1 x Baseline)
24.8 21.33 80% Zinc + 20% Carbon 4 0.00 21.33 2.36 0.94 0.14 9.03 50.00 83.02 (1.1 x Baseline)

Preliminary Conclusions/ Future Directions
- Various formulations of Calcium Zincate can be cycled with high 50% utilization of the active zinc material for more than 57+ ongoing cycles without capacity loss
- Understand the key factors during battery cycling at the nanoscale that led to the improved material utilization at high cycle life compared to metallic zinc
- Investigate hydrogen evolution reaction (HER) and possible additives to reduce zinc anode gassing
- Investigate calcium zincate anodes vs manganese dioxide (Zn-MnO₂) cells

Electrode Mixture Composition and Properties

Cell#1 Cell#2 Cell#3 Cell#4

Metallic Zinc | 3.2 | 3.2 | 3.2 | 3.2
Zinc Oxide | 5.61 | 5.61 | 5.61 | 5.61
Calcium Zincate | 2.59 | 2.59 | 2.59 | 2.59

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References:
(2) J. Vu et al. J. Power Sources 103 (2001) 93-97

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