Screening of Alkaline Battery Separators Using Anodic Stripping Voltammetry

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Rechargeable Alkaline Zn-MnO$_2$ Batteries

- MnO$_2$ • ~ $1-2$ per lb • Mn, 12$^{th}$ most abundant • 16,000,000 tons (2012) • Safe

- KOH • Potash ~ $260$ per ton • Abundant • Aqueous • > Safety than Li-org

- Zn • ~ $1$ per lb • 25$^{th}$ most abundant • 13,000,000 tons (2012) • Safe

<table>
<thead>
<tr>
<th>Element</th>
<th>Cost per lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>$13-15/lb</td>
</tr>
<tr>
<td>Li</td>
<td>$2.5/lb</td>
</tr>
<tr>
<td>V</td>
<td>$11-12/lb</td>
</tr>
<tr>
<td>Al</td>
<td>$0.8-0.9/lb</td>
</tr>
<tr>
<td>Ni</td>
<td>$6-9/lb</td>
</tr>
<tr>
<td>Cu</td>
<td>$2.5-3.5/lb</td>
</tr>
</tbody>
</table>

The ultimate challenge in Zn/MnO$_2$ batteries is reversibility to increase cell lifetime.
Rechargeable Alkaline Zn-MnO$_2$ Batteries

\[
\begin{align*}
\text{Mn}^{IV}O_2 + H_2O + e^- & \rightleftharpoons \text{Mn}^{III}OOH + OH^- & E^0 = 0.26 \text{ V (Hg/HgO)} \\
\text{Mn}^{III}OOH + H_2O + 3OH^- & \rightleftharpoons \text{Mn}^{III}(OH)_6^{3-} & E^0 = -0.38 \text{ V (Hg/HgO)} \\
\text{Mn}^{III}(OH)_6^{3-} + e^- & \rightleftharpoons \text{Mn}^{II}(OH)_2 + 4OH^- &
\end{align*}
\]
Failure Mechanisms of MnO$_2$ Cathode

1. Instability of Mn(III) resulting in formation of irreversible Mn$_3$O$_4$
2. Zn poisoning forming irreversible ZnMn$_2$O$_4$
Research by Ford in the 1980s showed that the MnO$_2$ cathode could be stabilized at low loadings in the absence of Zinc.

Full 2e$^-$ MnO$_2$ cathodes have been shown to be 100% reversible but only in the absence of Zinc thus there is an imperative need for Zinc/Zincate blocking separators.

Features of a Good Zn Battery Separator

Cathode

High Ionic Conductivity
Metric: Electrochemical Impedance

Low Zincate Permeability
Metric: Zinc Diffusion Coefficient

Separator

OH⁻, K⁺, or Na⁺

Zn(OH)₄²⁻

Zinc Electrode
Features of a Good Zn Battery Separator

High Ionic Conductivity
Metric: Electrochemical Impedance

Low Zincate Permeability
Metric: Zinc Diffusion Coefficient

A rapid screening method for the determination of Zn (zincate) membrane/separater permeability is needed
Sampling, Dilutions, and Calibration Solutions

- time intensive
- lots of glassware
- requires acidic solutions (2% HNO₃)
- requires total dissolved solids <0.2%
- huge dilution >300X
- expensive bulky equipment

Instrumentation

Perkin-Elmer
Inductively Coupled Plasma – Mass Spectrometer
Analysis Techniques – Complexometric Titration

**Colorimetric Titration w/EDTA**

- Difficult Endpoint Determination
- Requires pH ≤ 11
- Use of ammonium buffer
- Dilution >20X
- ppm limits of detection

**Instrumentation**

- Or
  - UV/Vis Spectrometer
  - Perkin-Elmer
Anodic Stripping Voltammetry (ASV)
-historically done on Hg drop electrodes
-done in buffered solutions

Sensitive
-limits of detection (LOD): ppb levels
Selective
-different metals are resolved by their stripping/oxidation potential

*Analyst, 2012, 137, pp. 614-617*
ASV with *in situ* Plated Bi Films

-Bi film electrodes increasingly replacing Hg

**Bi film electrodes**

- less toxic than Hg
- low sensitivity to dissolved oxygen
- better reproducibility
- no need for electrode conditioning

*in situ* Plated Bi Films

-Bi is plated onto an passive electrode with the element of interest
- During stripping, the element of interest is stripped from the Bi film

Typically done in buffered pH ~4 solutions due to insoluble metal oxides at higher pH levels
Alkaline Aqueous Chemistry (pH>14)

Insoluble metal oxides become soluble by hydroxide complexation

\[
\begin{align*}
\text{ZnO(s)} & + \text{H}_2\text{O} + 2\text{OH}^- & \rightarrow & \text{Zn(OH)}_4^{2-} \\
\text{PbO(s)} & + \text{H}_2\text{O} + \text{OH}^- & \rightarrow & \text{Pb(OH)}_3^- \\
\text{CdO(s)} & + \text{H}_2\text{O} + \text{OH}^- & \rightarrow & \text{Cd(OH)}_3^- \\
\text{Bi}_2\text{O}_3(s) & + 3\text{H}_2\text{O} + 2\text{OH}^- & \rightarrow & 2\text{Bi(OH)}_4^- 
\end{align*}
\]

This allows for the opportunity to use ASV to measure Zn ion species in highly alkaline environments for the first time

http://www.porexfiltration.com/learning-center/technology/precipitation-microfiltration/
Zinc ASV Curves for Various Films

Duay et al., Electroanalysis (2017) DOI:10.1002/elan.201700337
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Zinc stripping peak is only well-defined and Gaussian in the presence of Bi, Cd, and Pb….why?

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Zinc ASV Curves for Various Films

Zinc stripping peak is only well-defined and Gaussian in the presence of Bi, Cd, and Pb….why?

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Need for all three Cd, Pb, and Bi?

All three have been used as additives in battery grade Zn where ‘plating’ and ‘stripping’ of Zn is necessary

Cadmium (Cd)  
-increases hydrogen overpotential  
-known to alloy with Zn

Lead (Pb)  
-increases hydrogen overpotential  
-known as alternative ASV film to Bi

Bismuth (Bi)  
-increases hydrogen overpotential
Calibration Curves in KOH and NaOH

Linear Behavior of Zn Stripping Peak Area vs. Zn Concentration
Calibration Curves in KOH and NaOH

<table>
<thead>
<tr>
<th>Figures of Merit</th>
<th>30% NaOH</th>
<th>35% KOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn LOD (ppm)</td>
<td>2.9 ± 0.4</td>
<td>1.6 ± 0.6</td>
</tr>
<tr>
<td>Sensitivity (µC/ppm)</td>
<td>13.3 ± 1.8</td>
<td>31.8 ± 9.1</td>
</tr>
<tr>
<td>Solution Molarity (M)</td>
<td>10.2</td>
<td>7.07</td>
</tr>
<tr>
<td>Solution Conductivity (mS/cm)</td>
<td>~190</td>
<td>~620</td>
</tr>
</tbody>
</table>

Linear Behavior of Zn Stripping Peak Area vs. Zn Concentration

Duay et al., Electroanalysis (2017) DOI:10.1002/elan.201700337
Zincate Membrane Diffusion Rates

Measurements performed with 3-D printed polypropylene H-Cell
Special thanks to Eric Allcorn for help in designing and printing
**Zincate Membrane Diffusion Rates**

Testing of commercial-off-the-shelf membranes:
- Celgard 3501
- Cellophane 350P00

\[
D = \frac{V_b L}{A t} \ln \left( \frac{C_A}{C_A - C_B} \right)
\]

- **D**: diffusion coefficient of zinc
- **V_b**: volume of the draw solution
- **L**: thickness of the membrane
- **A**: exposed area of the membrane
- **t**: time elapsed
- **C_A**: concentration of zinc in the feed solution
- **C_B**: concentration of zincate in the draw solution.

*Duay et al., Electroanalysis (2017) DOI:10.1002/elan.201700337*
Zincate Membrane Diffusion Rates

Testing of commercial-off-the-shelf membranes:
- Celgard 3501
- Cellophane 350P00

\[ D = \frac{V_b}{bL} A t \ln \left( \frac{C_A}{C_B} \right) \]

**Note:** ICP/MS results are in the absence of Bi, Pb, and Cd in Solution.

Duay et al., *Electroanalysis* (2017) DOI:10.1002/elan.201700337
Zincate Membrane Diffusion Rates

Zincate Diffusion Coefficient results compare well to ICP-MS

\[
D = \frac{V_b \cdot L}{A \cdot t \cdot \ln \left( \frac{C_A}{C_B} \right)}
\]

With Bi, Pb, and Cd in Solution

Duay et al., Electroanalysis (2017) DOI: 10.1002/elan.201700337
### Comparison of ASV with Other Methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Dilution Factor</th>
<th>Method LOD (Method LOD x Dilution Factor)</th>
<th>Timeframe of Experiment</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASV (this work)</td>
<td>0</td>
<td>1.6 ± 0.6 ppm</td>
<td>Hours</td>
<td>No Dilution or Buffered pH Needed</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>&gt; 300x</td>
<td>25 ± 8 ppb*</td>
<td>Days</td>
<td>Need Acidified Solution with Total Dissolve Solids below 0.2%</td>
</tr>
<tr>
<td>Complexometric Titration</td>
<td>&gt; 20x</td>
<td>4.8 ± 1.2 ppm*</td>
<td>Weeks</td>
<td>Need Buffered pH Solution for Unambiguous Color Change</td>
</tr>
</tbody>
</table>

*Values obtained in our lab.

ASV has no need for dilution

ASV Experimental LOD is lower compared to other methods

Timeframe of ASV Experiments is Shorter

**ASV data is collected in real time with the lowest experimental limit of detection (LOD) for Zn**
Conclusions

- Anodic Stripping Voltammetry is used for the first time in high pH Conditions where Zn stripping peak is linear with Zn concentration were found
- Application towards Zn alkaline battery membranes was identified
- This method is used in situ which allows real time Zn sensing
- Zn diffusion coefficient results compare well to traditional ICP-MS methods

This method will be invaluable in the development and screening of new separators for advanced alkaline zinc batteries
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Questions?