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Anodic Stripping Voltammetry Detection of Bismuth, Copper and Zinc and its Role in Evaluating Battery Separators

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Background and Objectives

Aqueous alkaline batteries based on Zn anodes represent a viable option for energy storage due to their low cost, theoretically high energy densities, and material abundance. However, the partial solubility of Zn anodes – as well as Mn, Cu, and Bi based cathode materials – in the alkaline electrolyte leads to problems of active material loss, shorting, and electrode "poisoning" as inactive phases are formed. Here, we present the use of anodic stripping voltammetry (ASV) to measure the diffusion rates of dissolved metal ions through various battery separators in alkaline electrolyte, focusing on the most recently developed Bi assay.

Objectives

- **Develop a new anodic stripping voltammetry assay to quickly measure Bi concentration in highly alkaline (pH >14) KOH electrolyte.**
- **Apply the developed assay to gain unprecedented insight into the diffusion rate of Bi ions through alkaline battery separators.**

Solubility of Metals in Alkaline

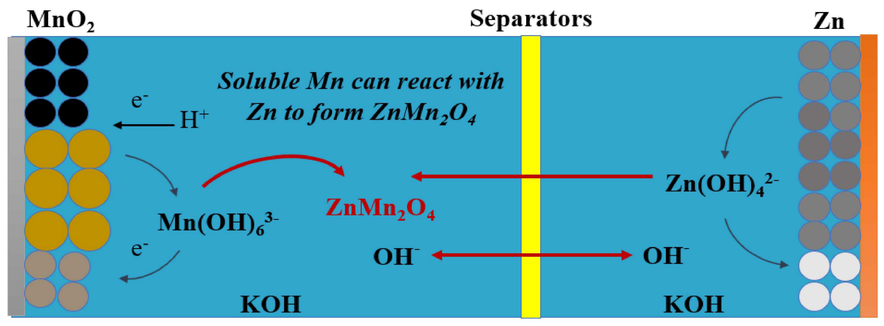
The electrode materials used in alkaline batteries are soluble in high pH electrolytes. Active material loss and dendrite formation are driven by dissolution and precipitating processes.

Metal Hydroxide Complexes Formed at High pH

$ZnO(s) + H_2O + 2OH^- \rightarrow Zn(OH)_4^{2-}$

$Bi_2O_3(s) + 3H_2O + 2OH^- \rightarrow 2Bi(OH)_4^-$

$CuO(s) + H_2O + 2OH^- \rightarrow Cu(OH)_4^{2-}$



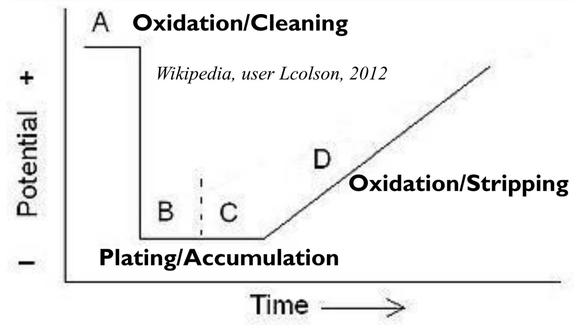
Adapted from J. Duay, et al. Electroanalysis (2017)

Metal Ion Measurement Techniques

- Inductively couples plasma mass spectrometry (ICP-MS) requires large dilution factors & low pH
- Complexometric titrations require long experiment times.
- ASV circumvents both issues as a rapid and sensitive method for metal ion sensing.

Method	Dilution Factor	Experiment Timeframe
ASV	0	Hours
ICP-MS	>300x	Days
Complexometric Titration	>20x	Weeks

Anodic Stripping Voltammetry

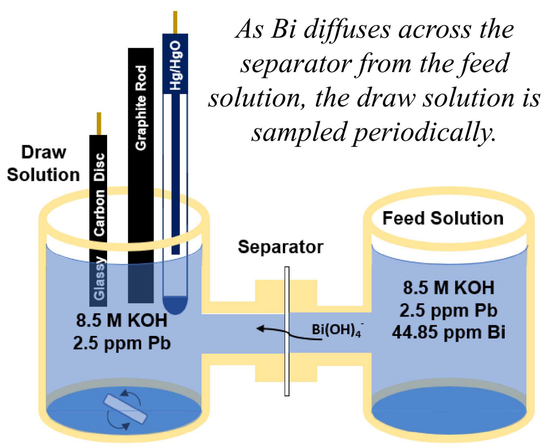


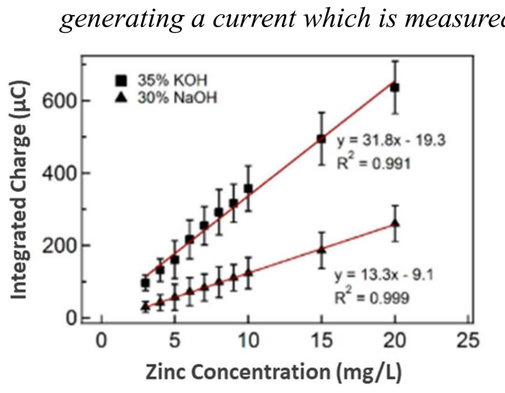
Testing Procedure

After an oxidative cleaning step, metal ions are plated onto the working electrode. Then, an oxidative potential is gradually applied, stripping the plated ions off the working electrode and generating a current which is measured.

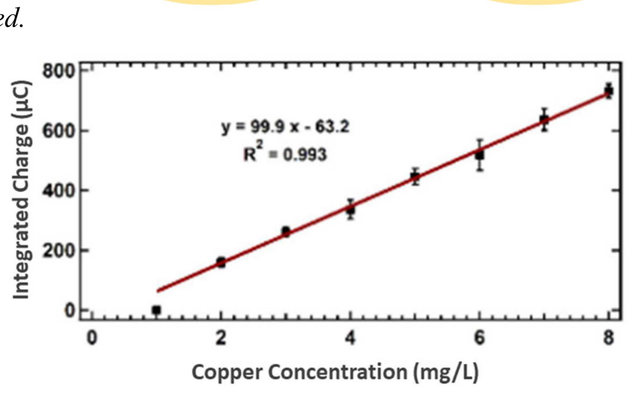
ASV Test Cell

As Bi diffuses across the separator from the feed solution, the draw solution is sampled periodically.



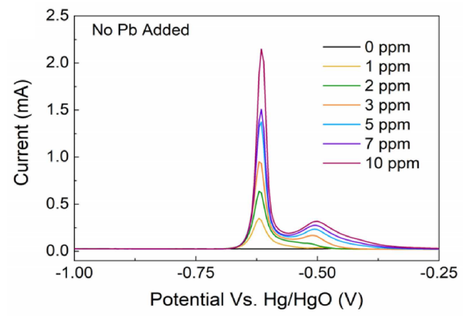


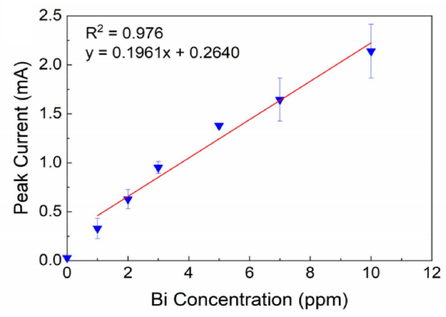
J. Duay, et al. *Electroanalysis* 29 (2017) 1-8.



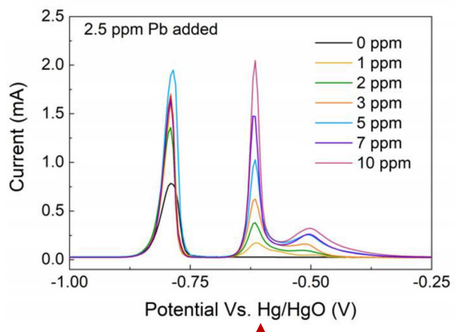
J. Duay, et al. *Electroanalysis* 29 (2017) 2685-2688.

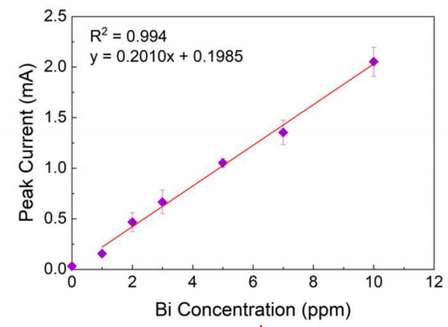
ASV for Bi Detection





Bi can be measured by itself in alkaline, however, the calibration curve we obtained was poorly linear. This prompted us to investigate the use of Pb as a stripping mediator:



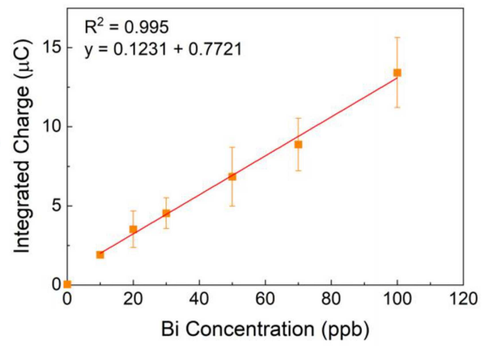


A Pb mediator improves the linearity and repeatability of the calibration curve. Pb and Bi form an alloy on the electrode surface.

ppb-Level Testing

Testing at ppb-level concentrations was used to determine the sensitivity of the method. Using the integrated charge instead of peak current gives more consistent results at ppb concentrations.

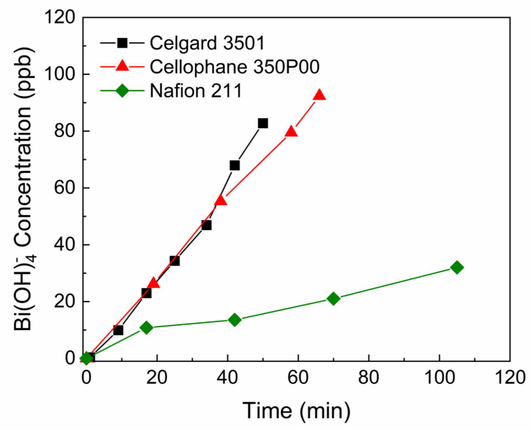
Limit of Detection (LOD) = 8.5 ppb



Separator Testing

Battery separators which slow the rate of Bi diffusion – like Nafion 211 shown here – will increase cycle life by limiting active material loss and shorting.

Separator	D_{Bi} ($cm^2\ min^{-1}$) x10^6
Celgard 3501	2.3 ± 0.2
Cellophane 350P00	1.9 ± 0.8
Nafion 211	0.45 ± 0.07



Conclusions and Research Output

The development of ion selective separators for aqueous alkaline batteries has the potential to greatly improve cycle life by limiting active material loss and shorting issues. The goal of this work was to develop a new method to quickly screen these alkaline battery separators for their diffusion properties.

- An innovative ASV methodology was developed for rapid measurement of Bi concentration in highly alkaline KOH electrolyte, replacing traditional ICP-MS and titration techniques.
- A Pb mediator in solution assisted with Bi plating and stripping to achieve a LOD of 8.5 ppb.
- The Bi diffusion rate through commercial battery separators was determined to demonstrate the application of ASV and to provide insight into their ability to prevent active material loss and shorting.
- Application of ASV for Zn, Cu, and now Bi, will be used to aid in the development of selective separators for alkaline battery development.

Publication:

- D.J. Arnot, T.N. Lambert. *Electroanalysis*, (2020). <*Submitted*>

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