SCREENING OF ALKALINE ZINC BATTERY SEPARATORS USING ANODIC STRIPPING VOLTAMMETRY

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Zinc alkaline battery chemistries such as Zn/Ni, Zn/MnO$_2$, and Zn/Air are currently attracting a lot of attention due to their potential as safe, low cost, high energy density rechargeable batteries. A main failure mechanism for these cells is the poisoning of the cathode material during cycling due to "zinc crossover". Advanced separators that successfully stop or limit this "zinc crossover" are crucial in order to increase the cycle lifetimes of these batteries. To be screened effectively, these membranes need to be evaluated for their ability to block zincate, the ionic form of zinc in strongly alkaline solutions (pH > 14). Here, an anodic stripping voltammetry (ASV) sensing assay is presented which provides *real time* determination of zincate transport in alkaline electrolyte with total experimental times on the order of hours. The obtained zincate diffusion coefficients for both ASV and elemental analysis techniques are shown to compare favorably.

Keywords: Alkaline Battery Separator · Zincate Transport · Celgard · Cellophane · Anodic Stripping Voltammetry

INTRODUCTION

Zn/Ni, Zn/MnO$_2$, and Zn/Air alkaline batteries are currently attracting a lot of attention due to their potential as safe, low cost, high energy density rechargeable batteries.[2] Current research focuses on progressing their cycle ability into thousands of cycles for their potential use in grid energy storage and military applications.[3-5]

A main failure mechanism for these cells is the poisoning of the cathode material during cycling due to "Zn crossover".[3-4, 6] Whereas, Zn transports across the separator membrane and combines with the cathode materials to produce irreversible phases. Advanced separators that successfully stop or limit this "zinc crossover" are crucial in order to increase the cycle lifetimes of these batteries.

To be screened effectively, these membranes need to be evaluated for their ability to block zincate, the ionic form of zinc in strongly alkaline solutions (pH > 14). Existing complexometric titration (EDTA *etc.*) and elemental analysis (ICP-MS *etc.*) methods for zincate membrane transport characterization require large sample dilution factors and additional sample processing which can take days to weeks to process as well as require high initial concentrations of zincate. Here, an anodic stripping voltammetry (ASV) sensing assay is presented which provides *real time* determination of zincate transport in alkaline electrolyte with total experimental times on the order of hours. The results presented here have been previously published.[1]

RESULTS AND DISCUSSION

Figure 1a represents the H-cell utilized here which consists of two solutions (feed and draw) separated by the membrane of interest with the feed side containing a known concentration of zincate and the draw side containing an initial blank electrolyte where the ASV is performed. This method allows the experiment to be performed *in situ* and thus eliminates the need for sample dilution and post experiment sample processing. For example, traditional ICP-MS measurements require total dissolved solids of less than 0.2% as well as acidified solutions. For 35% KOH samples (35% dissolved solids), this require dilution and then neutralization of the base which results in dilution factors >300x. Please see table 1 for a comparison of different methods. Thus, this electrochemical assay significantly increases the throughput for the screening of these vital membranes. To evaluate the utility of this assay, zincate diffusion through commercial off-the-shelf (COTS) Celgard 3501 and Cellophane 350P00 membranes is monitored using both ASV and inductively coupled plasma – mass spectrometry (ICP-MS) methods.

Figure 1b demonstrates the concentrations of Zn detected as a function of time through both the cellophane and Celgard separator in both NaOH and KOH solutions. It should be noted that there is a delay between the start of the experiment and when the Zn species is first detected. This is believed to be due to either the wettability of the separator and/or osmotic movement of the solvent due to the concentration gradient. All data processing was done only when the curves become linear
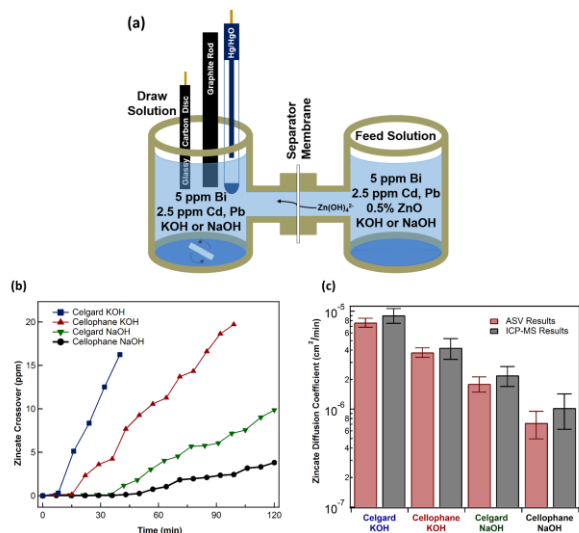
Figure 1. (a) Schematic of ASV H-cell setup. (b) $Zn(OH)_4^{2-}$ crossover concentration versus time for Celgard and Cellophane membranes in KOH and NaOH. (c) $Zn(OH)_4^{2-}$ diffusion coefficients calculated using crossover concentration versus time for both ASV and ICP-MS measurements. (Reproduced with permission from [1])

with respect to time. The greater the slope of these curves indicates more permeability to Zn and thus greater diffusion coefficients of Zn for the membrane.

Using the information from figure 1b, the diffusion coefficients in Figure 1C were determined. It is demonstrated that there is a larger diffusion coefficient for Zn through Celgard versus Cellophane for both NaOH and KOH electrolytes. Cellophane typically has a smaller porous structure and is more negatively charged than Celgard.[7] Thus, the smaller more negatively charged pores of Cellophane are thought to be more slightly more selective at partitioning the negatively charged Zn molecule.

Additionally, a larger diffusion coefficient was observed when KOH was used in place of NaOH. It is believed that the larger conductivity of KOH vs NaOH may be playing a large role. Where, assuming a similar membrane ionic selectivity between the two electrolytes, the higher conducting KOH electrolyte would have more free ions in solution which can screen the membrane charges in the pores, thus reducing any coulombic repulsion experienced by the Zn ions and subsequently allow additional transport of the Zn ions through the membrane.

Figure 1c compares the results obtained throught ASV with those obtained through ICP-MS. Even though the experiments are done over different sampling time domains (minutes for ASV and hours for ICP-MS), the values compare favourably across each membrane and electrolyte.

As different membranes can vary their Zn transport coefficients over many orders of magnitude, this sensing technique should play a major role in the rapid screening of membrane separators for Zn batteries.

Table 1. Comparison of Methods for the Experimental Limit of Detection (LOD) of Zincate Transport Across Battery Separator Membranes (reproduced with permission from [1])

Method	Dilution Factor	Method LOD [a]	Experimental LOD [b]
ASV (this work)	0	1.6 ± 0.6 ppm	1.6 ± 0.6 ppm
ICP-MS	> 300x	0.003 ppb[8] 25 ± 8 ppb*	0.009 ppm 7.5 ± 2.4 ppm*
Complexometric Titration	> 20x	100 ppb 4.8 ± 1.2 ppm*	1 ppm 96 ± 24 ppm*

[a] LOD for $Zn(OH)_4^{2-}$ in 35% KOH.
[b] LOD multiplied by dilution factor
*LODs obtained in our lab.

CONCLUSIONS

Anodic stripping voltammetry (ASV) is demonstrated here as a *real time* sensing technique for the rapid screening of advanced Zn alkaline battery separator membranes.

The ASV method was evaluated by monitoring Zn transport through two commercial separators, Celgard 3501 and Cellophane 350P00, and comparing it to a traditional ICP-MS method. The accuracy and precision of the Zn diffusion coefficients obtained through ASV compares very well with ICP-MS. ASV has an additional advantage with shorter experimental times and no need for sample post-processing when compared to ICP-MS and complexometric titration. This method will be invaluable in the development and screening of new separators for advanced alkaline Zn batteries.

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