

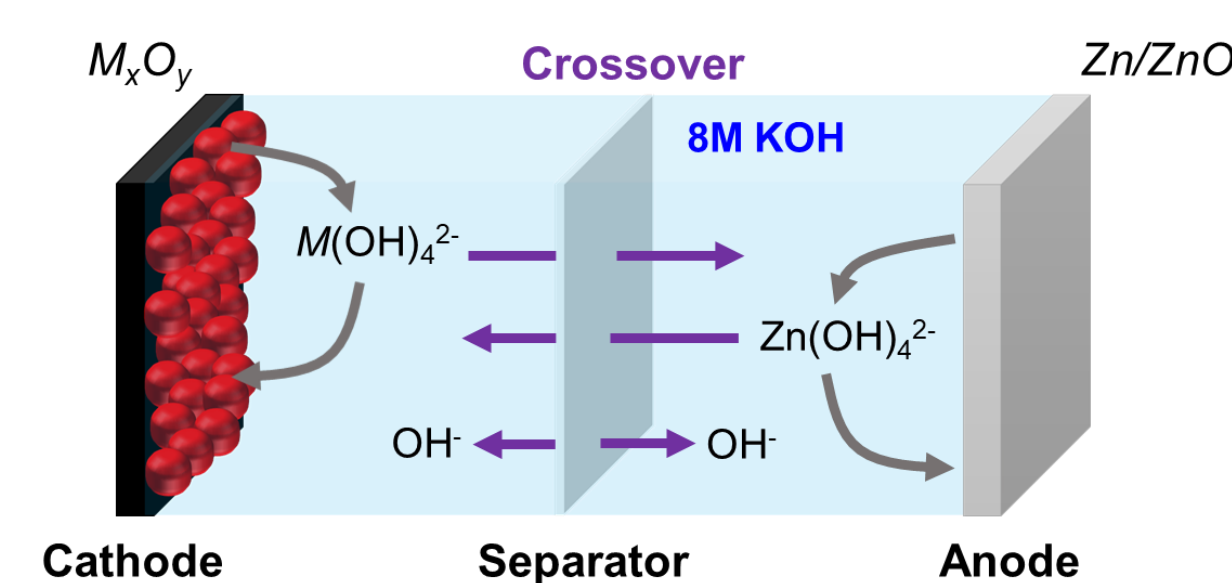
Metal Ion Sensing and Quantification by Anodic Stripping Voltammetry (ASV) for Study of Alkaline Battery Separators

Bryan R. Wygant¹, Jinchao Huang^{2,3}, Gautum Yadav^{2,3}, Damon Turney², Jungsang Cho², Michael Nyce², Sanjoy Banerjee^{2,3}, Timothy N. Lambert¹

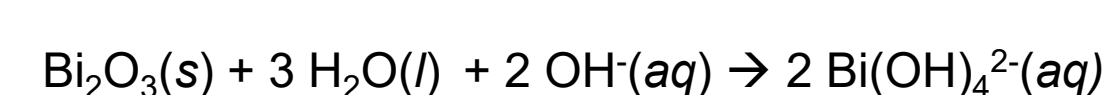
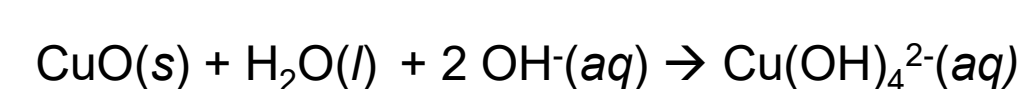
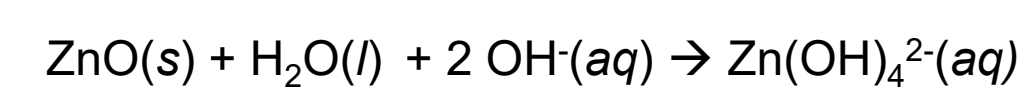
¹Department of Photovoltaics & Materials Technologies, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA; ²Department of Chemical Engineering, CUNY Energy Institute, The City College of New York, New York, New York 10031, USA; ³Urban Electric Power, Pearl River, New York 10965, USA

Background

- Aqueous alkaline batteries are a promising energy storage solution
 - High theoretical energy density, abundant materials (Zn, Mn, Cu, etc.), low flammability
- Suffer from solubility of many metals in highly alkaline solutions
 - Membranes in batteries can be used to limit diffusion



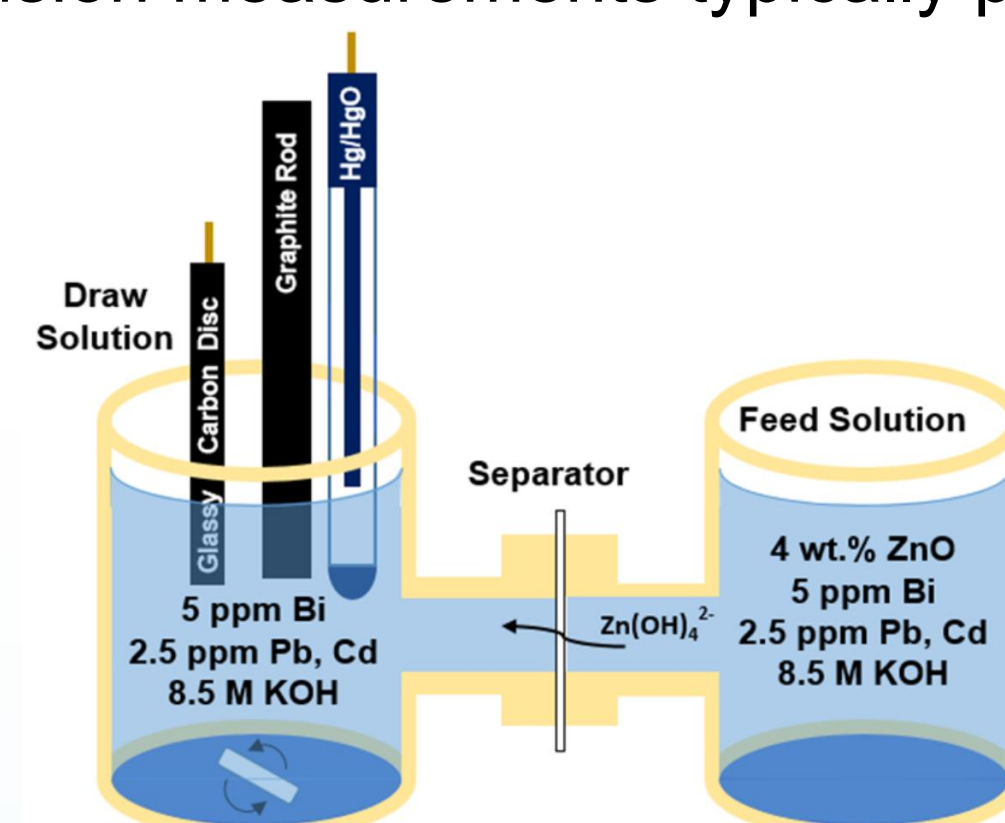
Common Metal Hydroxide Complexes



- Anodic stripping voltammetry (ASV) is a valuable tool for analyzing metal ion solubility and diffusion through membranes

ASV Measurement Conditions

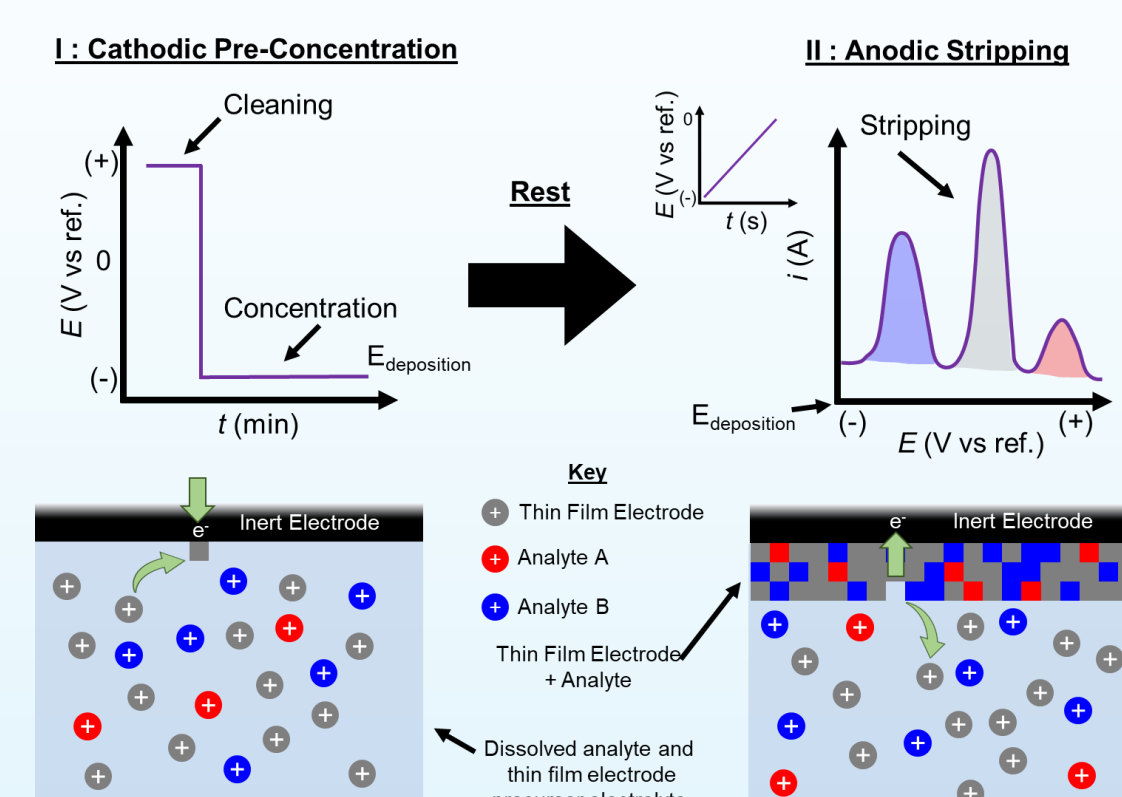
- ASV for ion diffusion measurements typically performed in H-cell



Adapted from Annot et al., Adv. Energy Mater., 2021, 11, 2101594

- Measurement consists of two steps:
 - Cathodic Deposition
 - Anodic Stripping

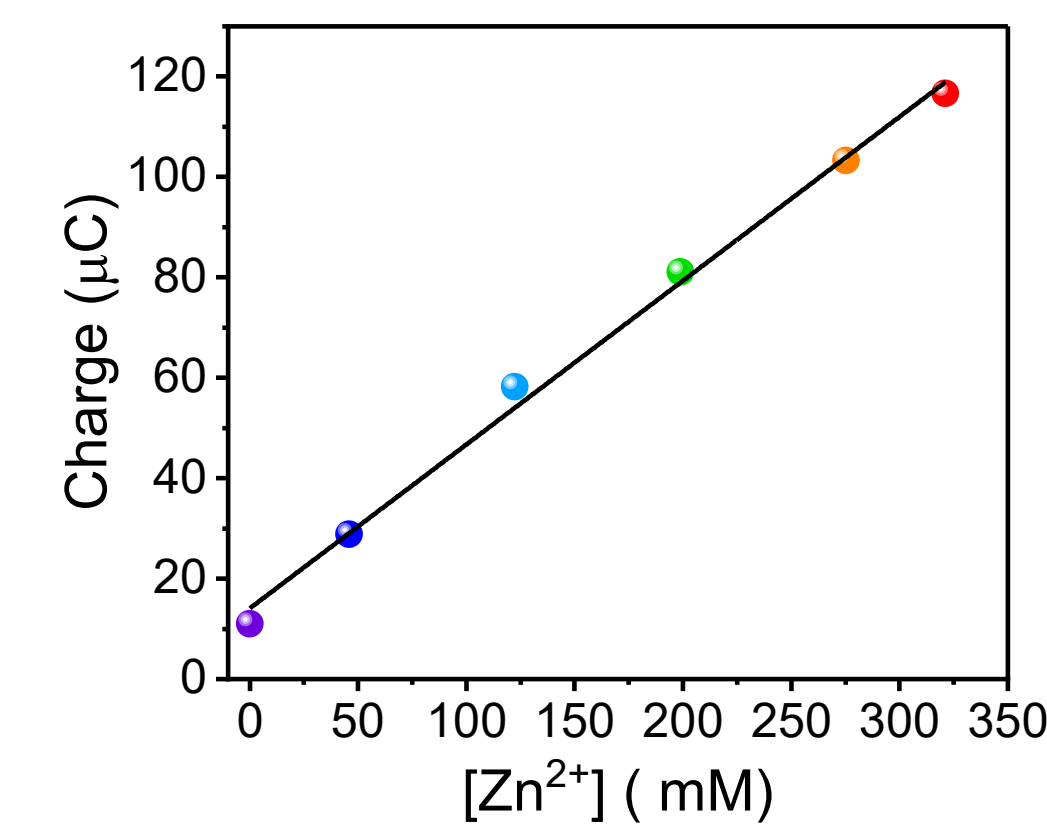
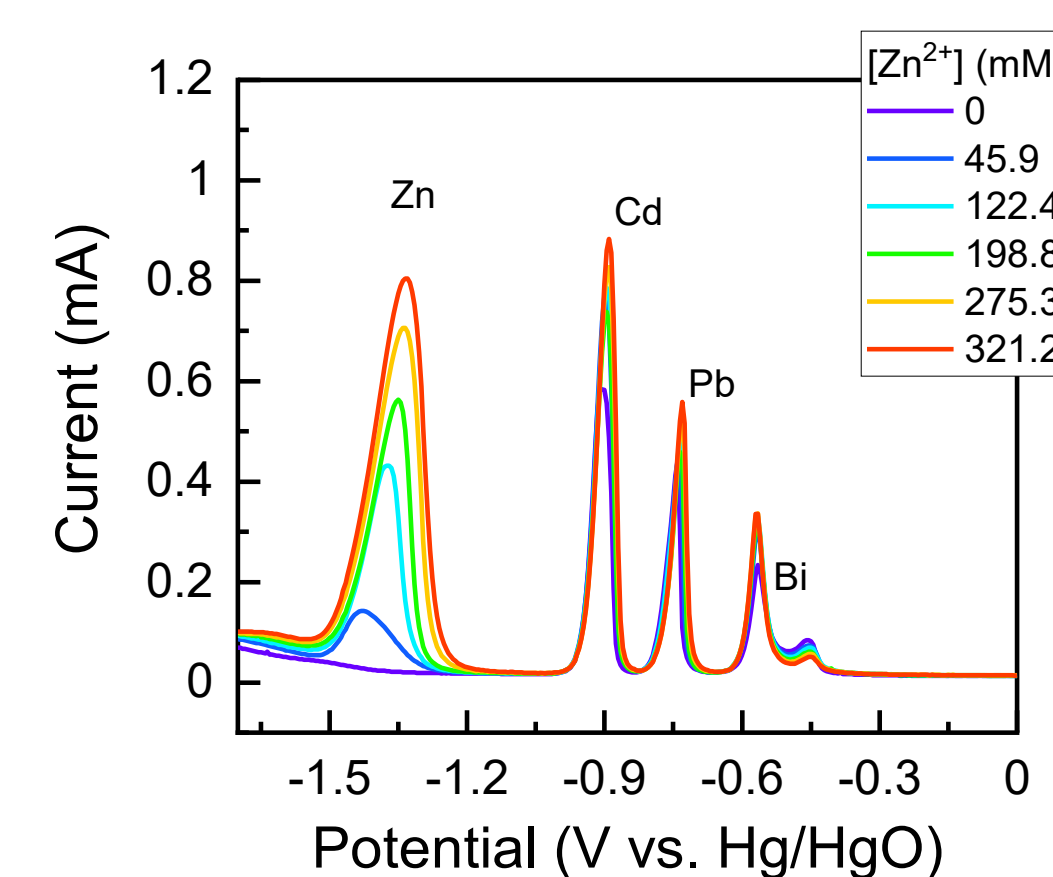
- A metal thin film electrode (typically Bi) is used for ASV and deposited from solution with the analytes



Adapted from Wygant et al., Front. Chem., 2022, 9, 1-8

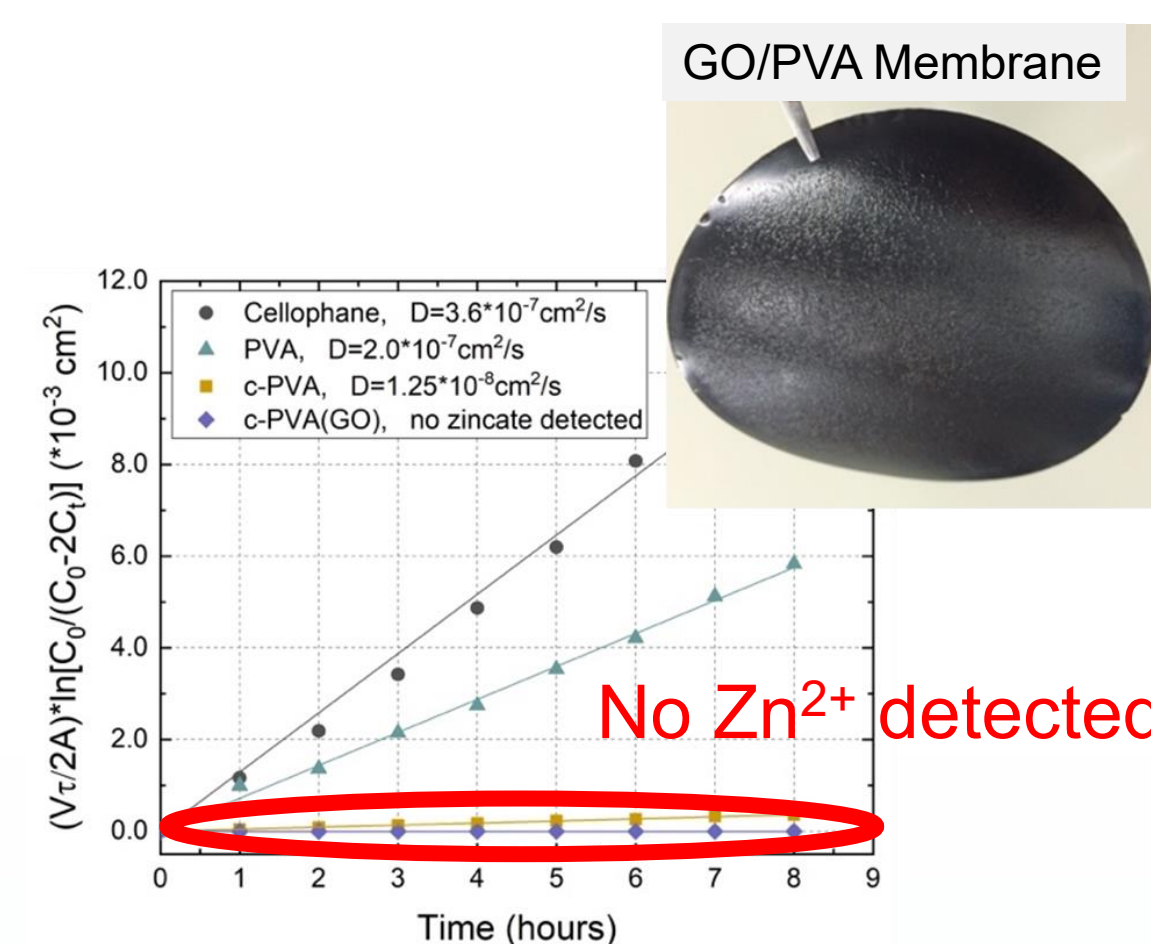
Calibration and Analysis

- Standard addition used to generate calibration curve for analyte of interest, allowing determination of species concentration



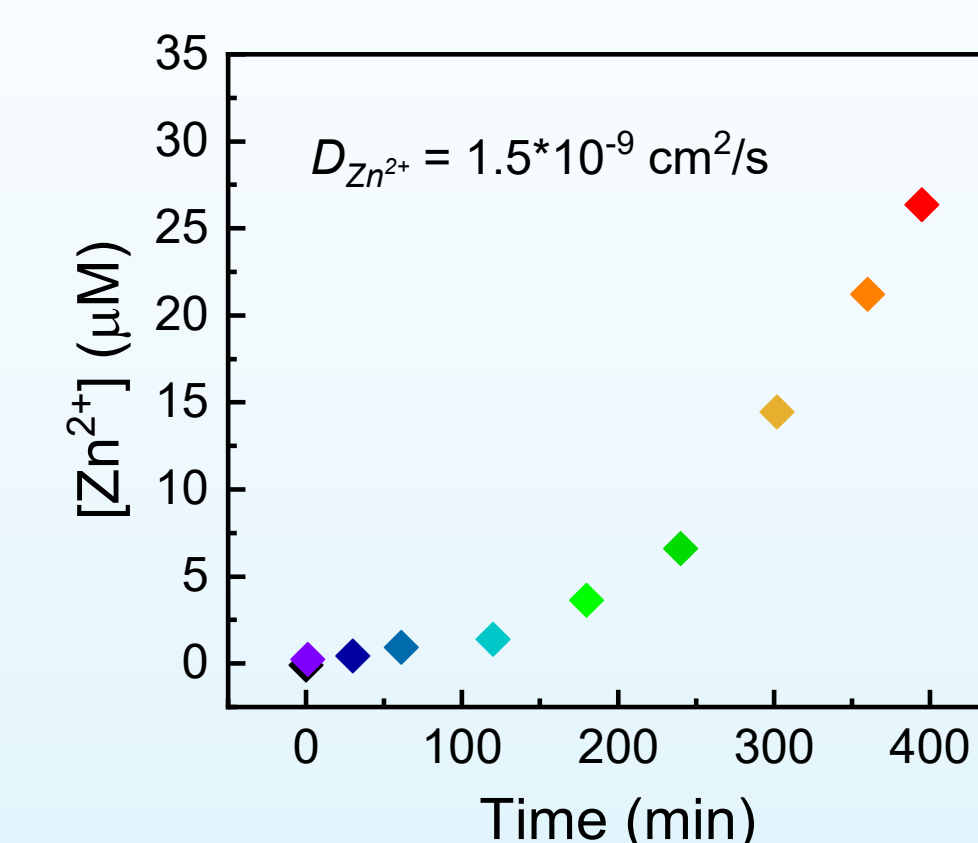
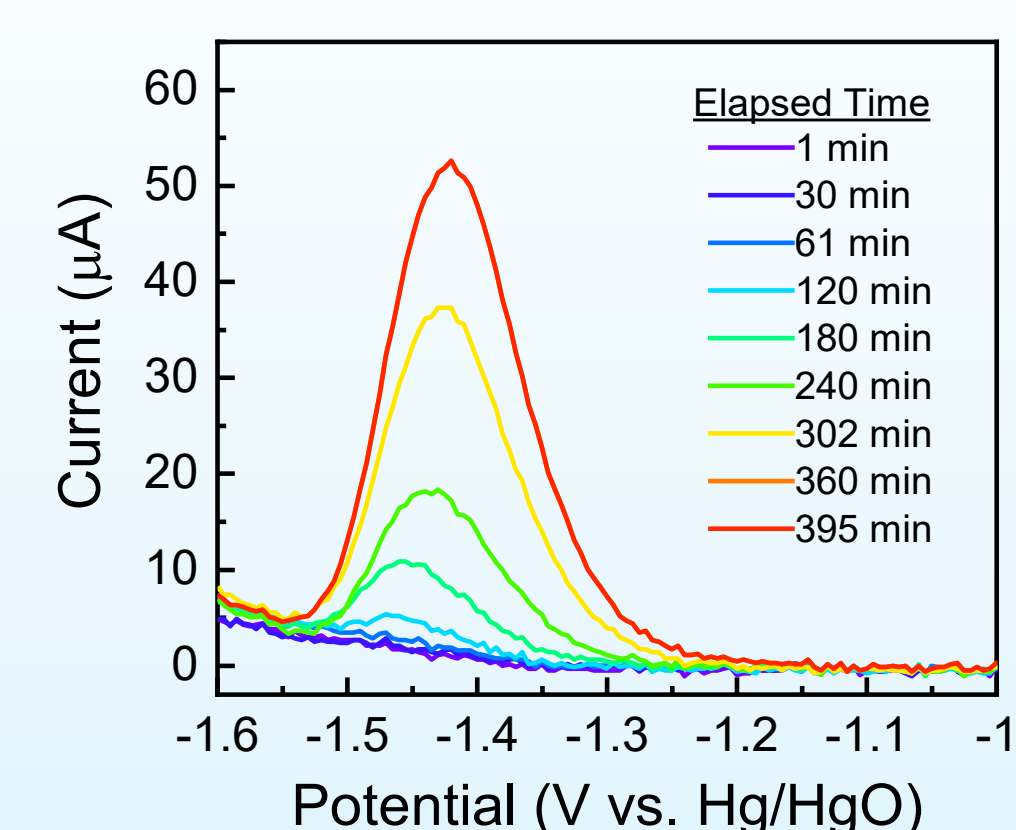
Zn Diffusion through GO/PVA

- Graphene oxide/polyvinyl alcohol (GO/PVA) is a promising ion-selective separator for alkaline batteries
 - Negligible Zn diffusion measured by complexometric titration over 8 hrs.



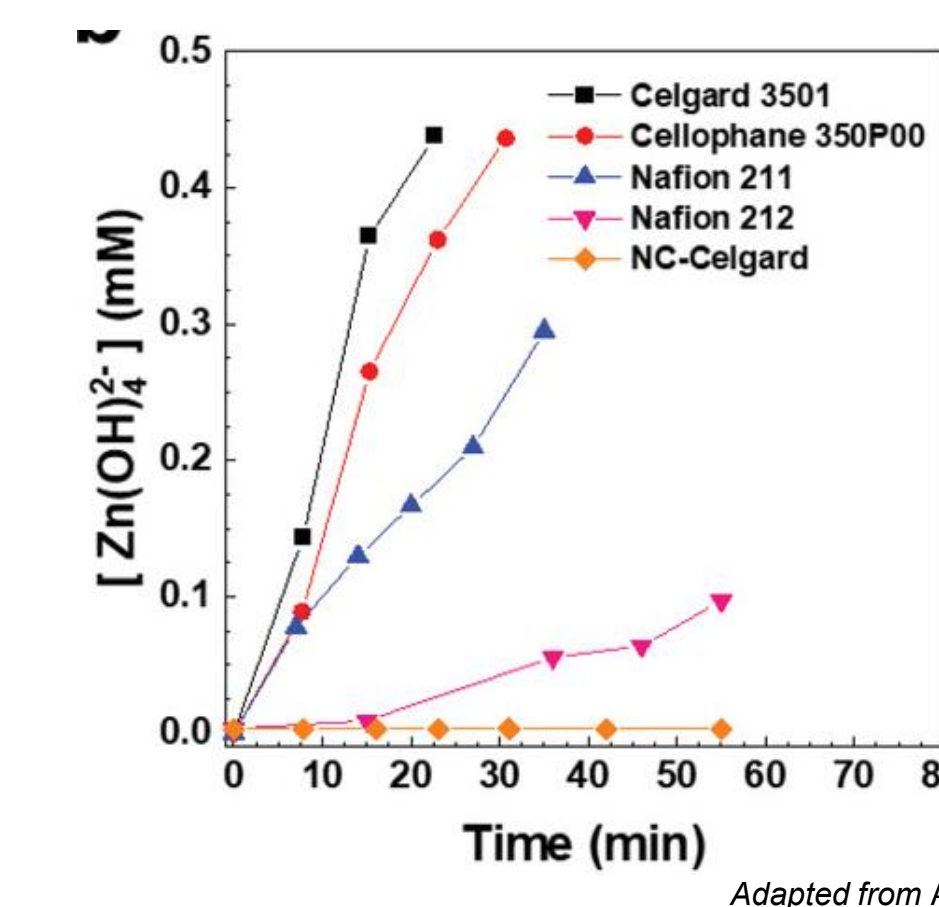
adapted from Huang et al., ACS Appl. Energy Mater. 2022, 5, 9952-9961

- The high sensitivity of ASV allowed for the calculation of Zn diffusion where titration had failed

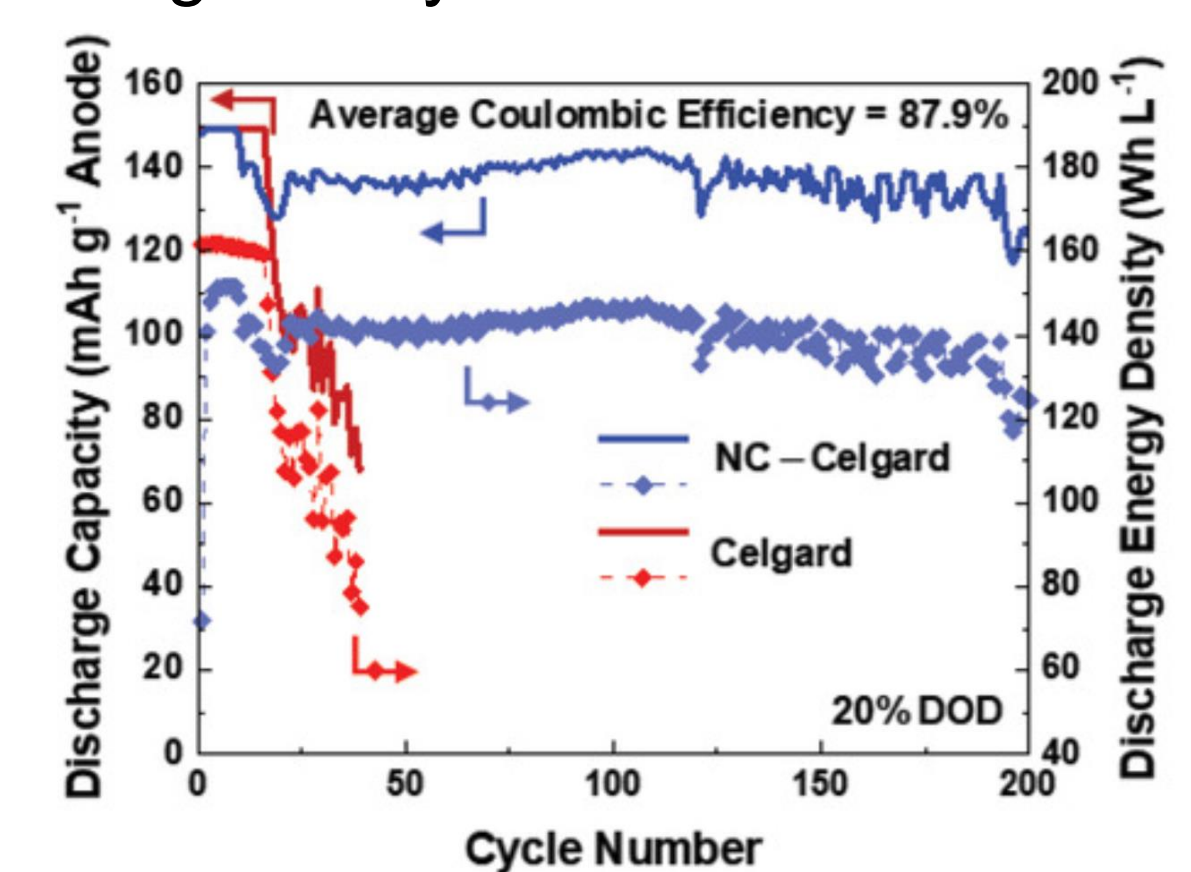


Additional Membrane Studies

- ASV aids in the development of ion-selective membranes for use in Zn-based alkaline batteries, improving battery life



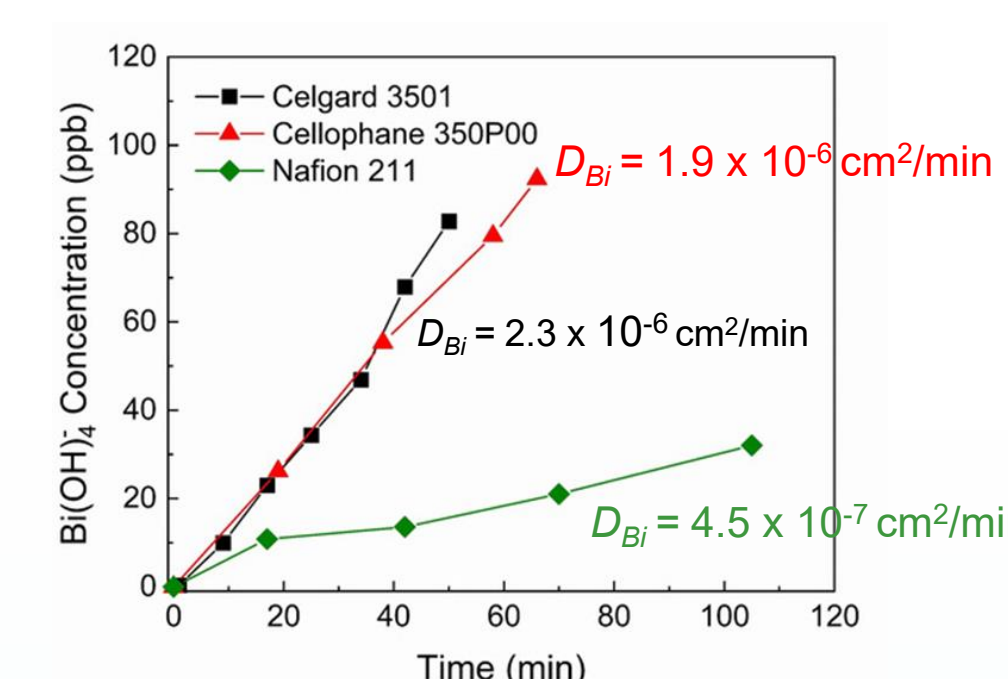
Adapted from Annot et al., Adv. Energy Mater., 2021, 11, 2101594



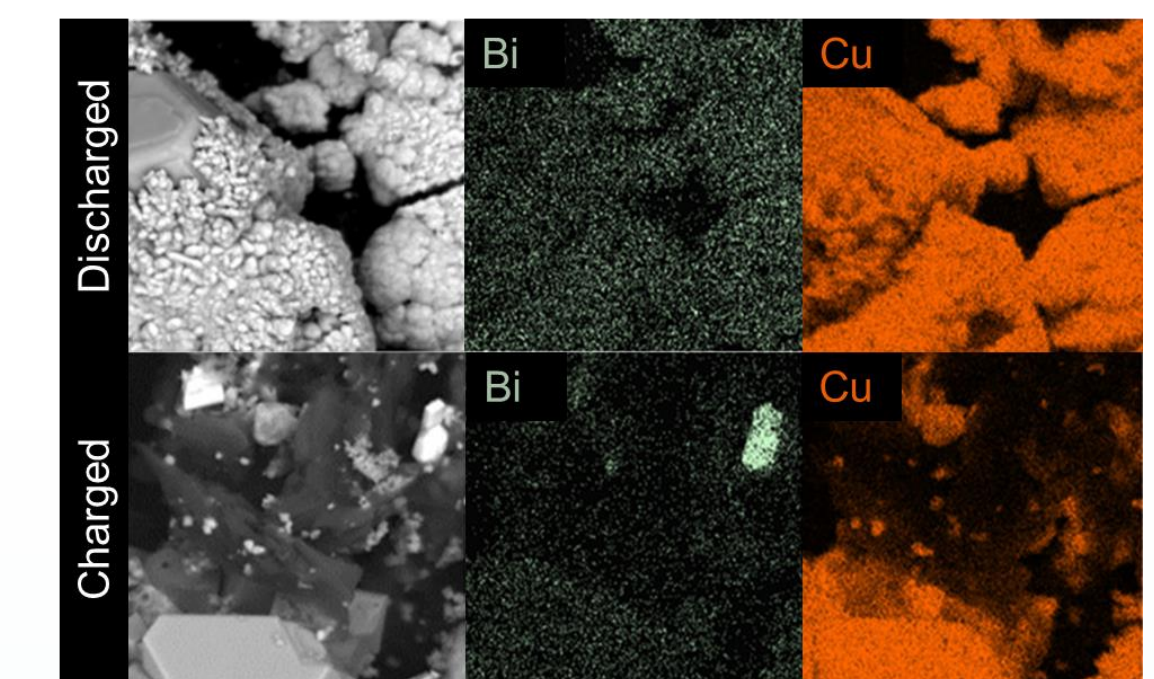
Membrane	D_{Zn} (cm ² /min)
Celgard 3501	5.7×10^{-6}
Nafion 211	5.0×10^{-7}
GO/PVA	1.5×10^{-9}
NC-Celgard	$< 1.0 \times 10^{-10}$

- Nafion-coated celgard (NC-Celgard) is a 100% selective separator that leads to an increase in Zn battery life

- ASV can also applied be used to measure diffusion of other species important to secondary alkaline batteries, like Bi
 - Used to enable rechargeability in Zn/CuO batteries



Adapted from Annot et al., Electroanalysis, 2021, 33, 797-803



Adapted from Schorr et al., ACS Appl. Energy Mater. 2021, 4, 7073-7082

Conclusions

- ASV allows for simple, fast measurements of metal ion concentration in highly alkaline solutions
- ASV enables more rapid development and analysis of Zn-selective membranes to improve battery lifetime by limiting Zn-diffusion
- ASV can be used to calculate diffusion coefficients of other metals (Bi, Cu) of importance to alkaline battery chemistries under development