

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

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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

$$\text{ZnO(s)} + \text{H}_2\text{O(l)} + 2 \text{OH}^-(\text{aq}) \rightarrow \text{Zn(OH)}_4^{2-}(\text{aq})$$

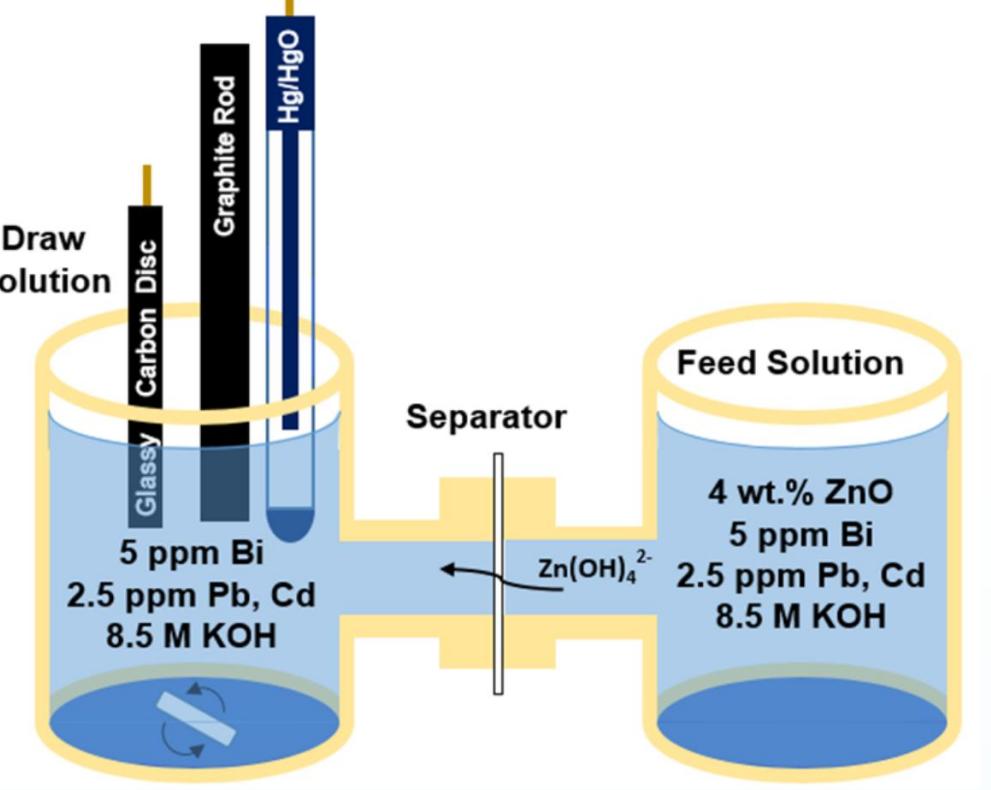
$$\text{CuO(s)} + \text{H}_2\text{O(l)} + 2 \text{OH}^-(\text{aq}) \rightarrow \text{Cu(OH)}_4^{2-}(\text{aq})$$

$$\text{Bi}_2\text{O}_3(\text{s}) + 3 \text{H}_2\text{O(l)} + 2 \text{OH}^-(\text{aq}) \rightarrow 2 \text{Bi(OH)}_4^{2-}(\text{aq})$$

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

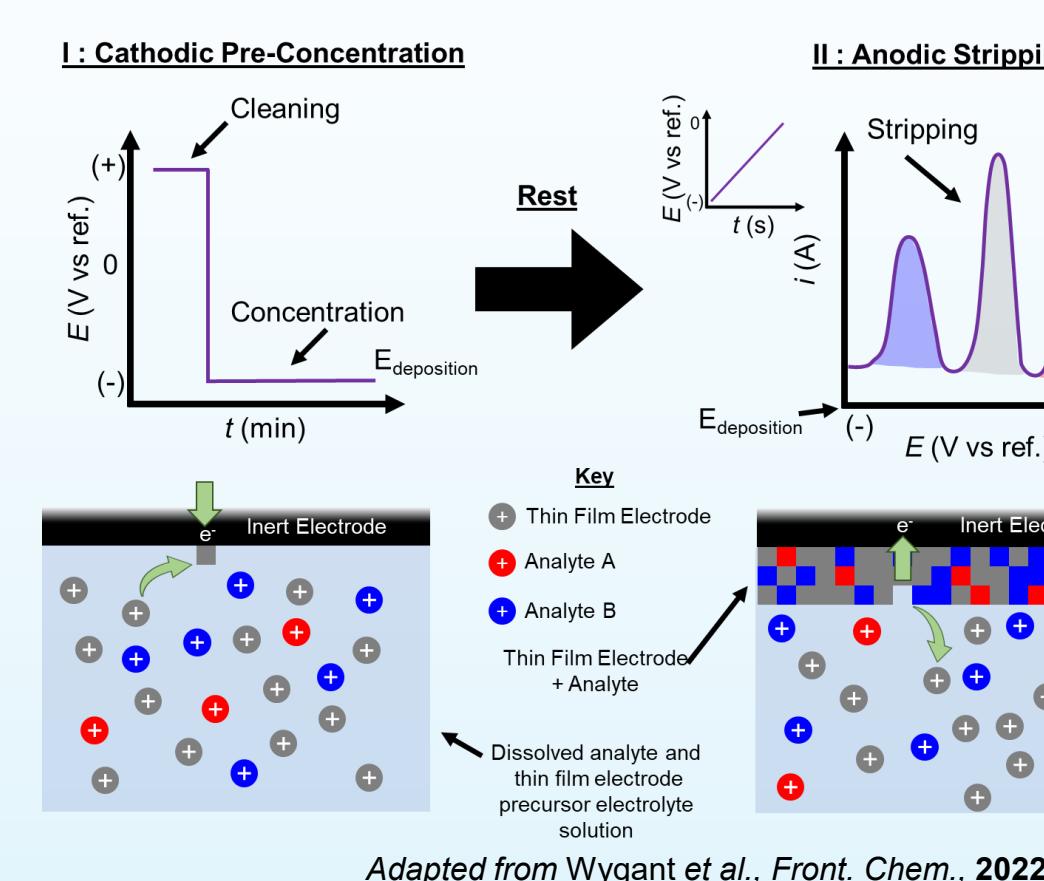
ASV Measurement Conditions

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



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

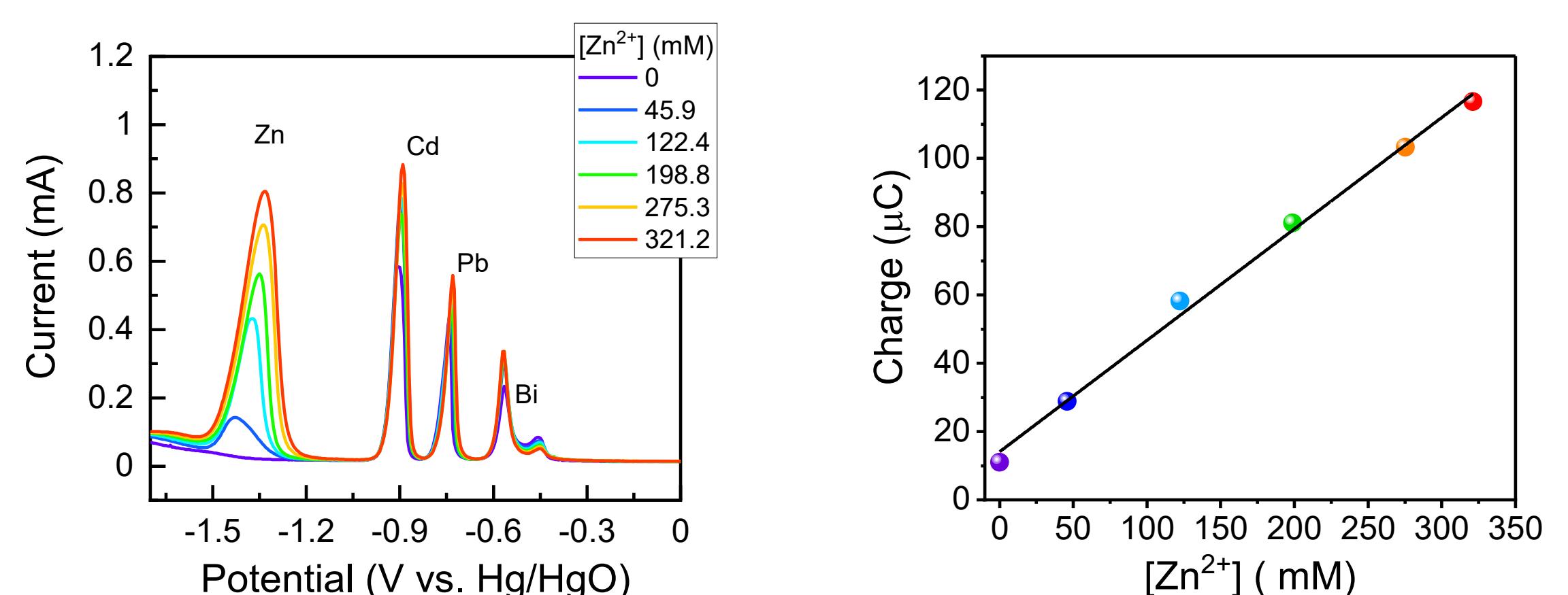
- Measurement consists of two steps:
 - Cathodic Deposition
 - Anodic Stripping
- A metal thin film electrode (typically Bi) is used for ASV and deposited from solution with the analytes



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

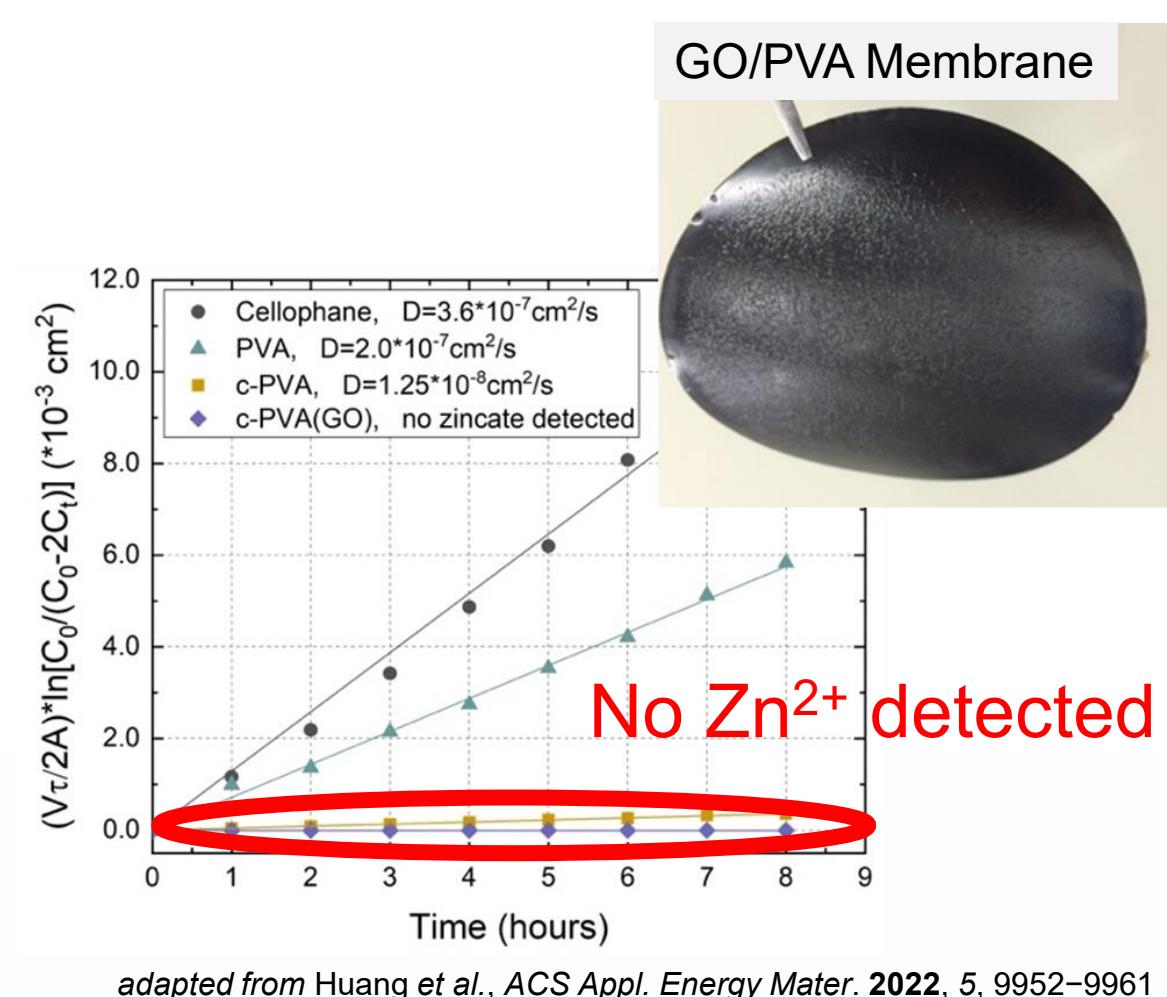
Calibration and Analysis

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

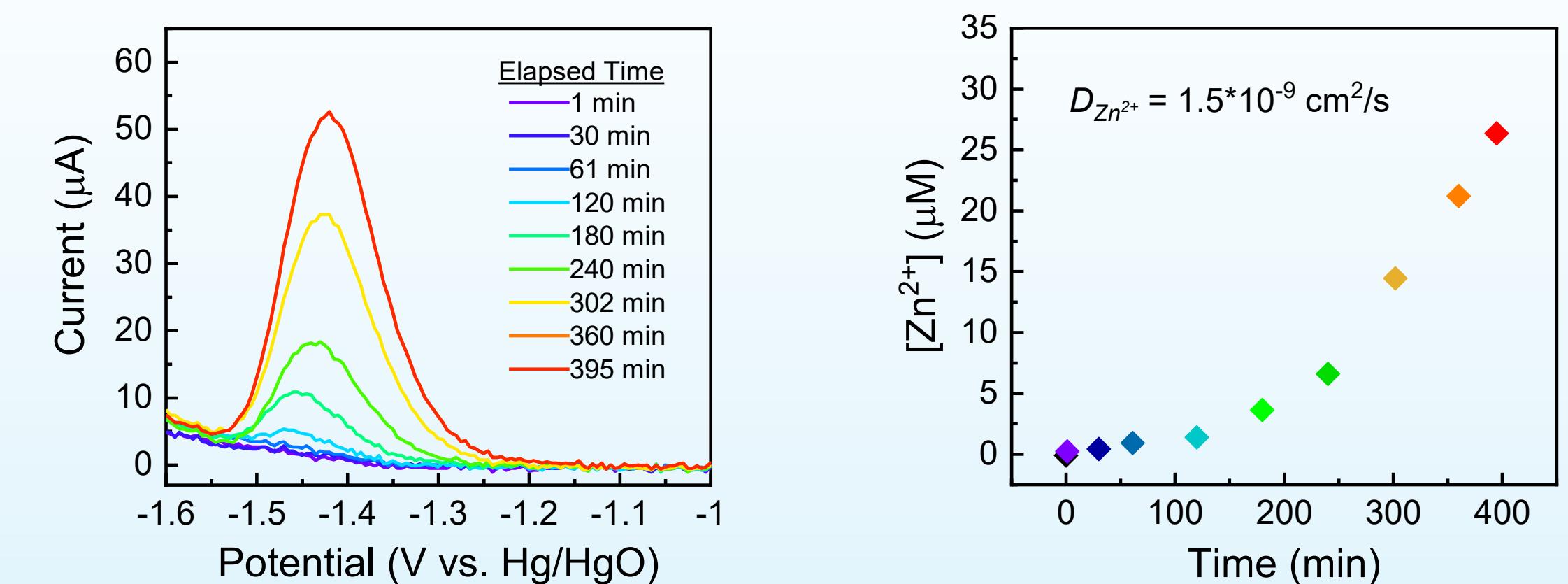


Zn Diffusion through GO/PVA

- 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.



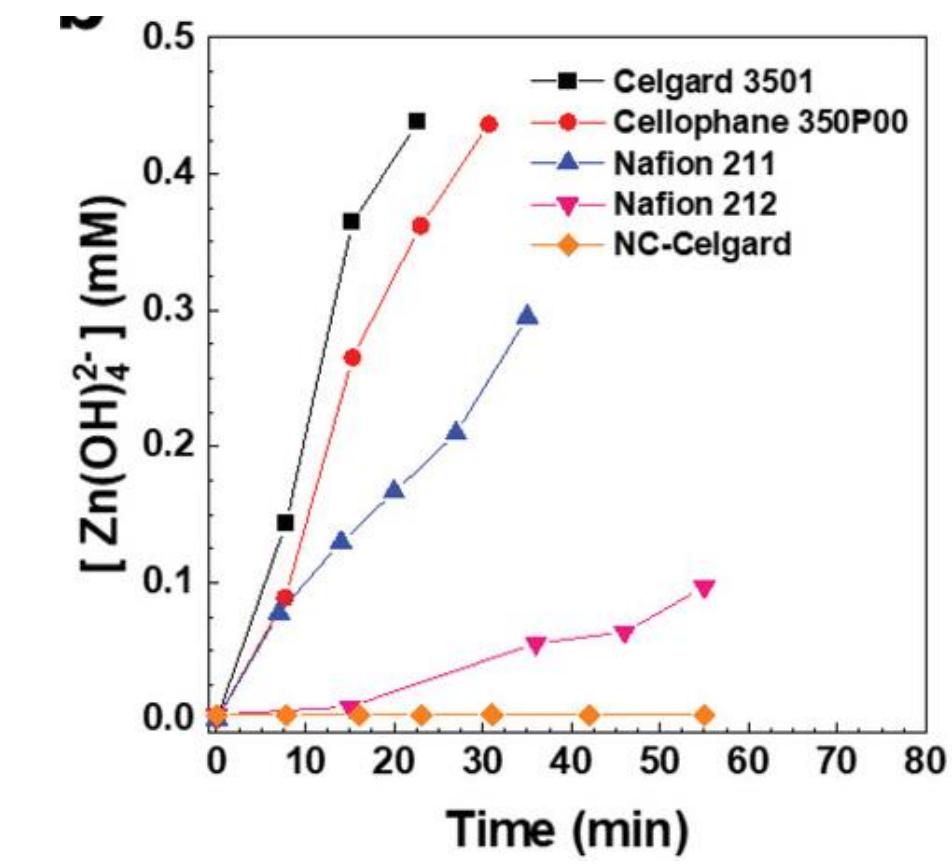
- The high sensitivity of ASV allowed for the calculation of Zn diffusion where titration had failed



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Additional Membrane Studies

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



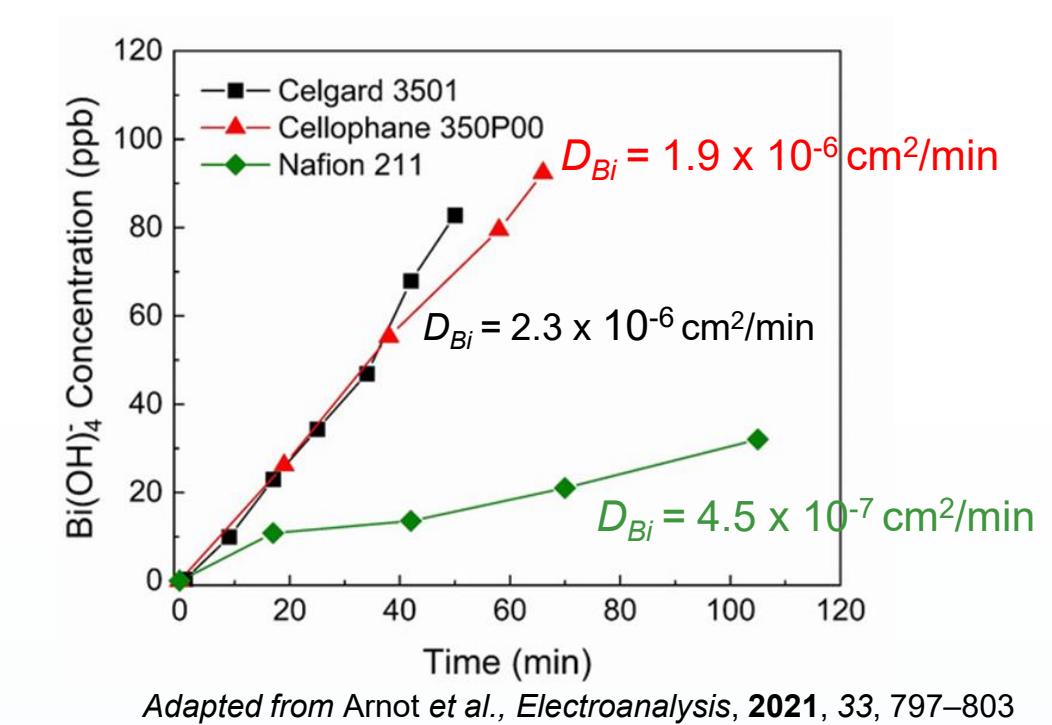
Adapted from Arnott et al., *Adv. Energy Mater.*, 2021, 11, 2101594

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	$< 1.0 \times 10^{-10}$

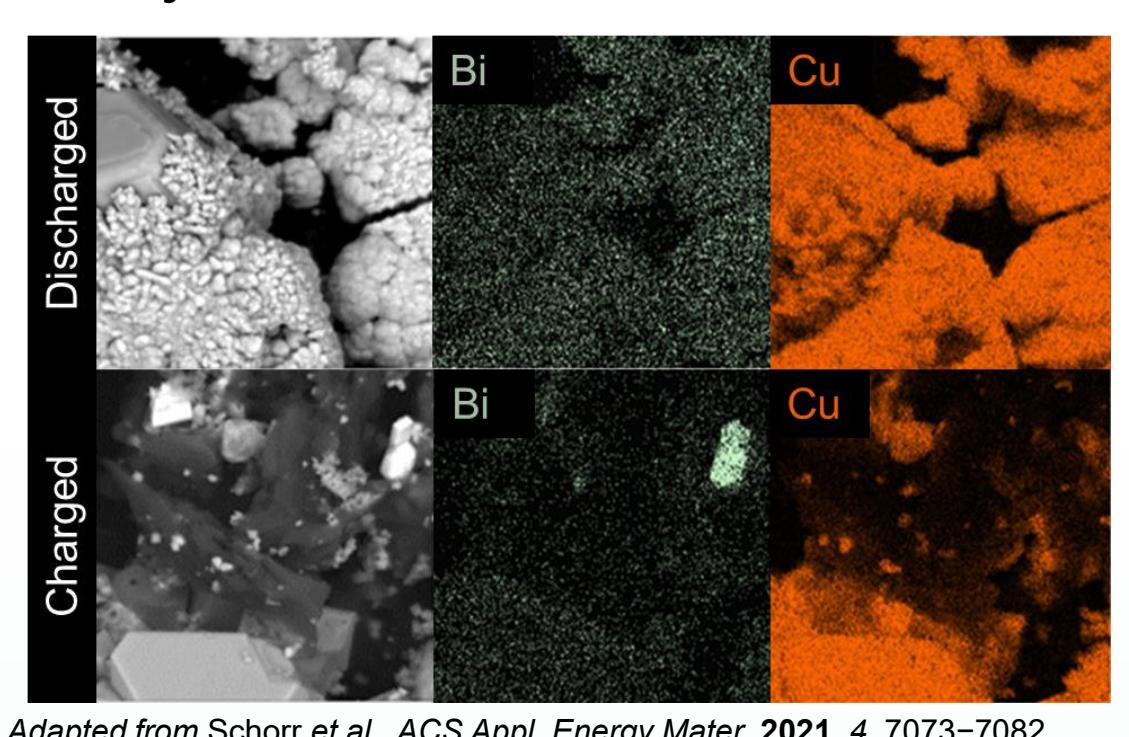
- Nafion-coated celgard (NC-Celgard) is a 100% selective separator that leads to an increase in Zn battery life

- ASV can also 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 Arnott 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