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DOE, OE ENERGY STORAGE PEER REVIEW

Design of Gel Polymer Electrolytes and Performance Assessment of Electrocatalysts for Durable Zn–Air Batteries

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August 5-7, 2025

U.S. DEPARTMENT of ENERGY

Project Overview

- **Project Goal:** Develop a low-cost, critical-material-free, multifunctional zinc-air battery (ZAB) prototype for long-duration energy storage.

- **Current Practice:** Solid-state Zn-air cells suffer from short lifespan, low energy efficiency, irreversibility, poor catalytic activity and lack of bifunctional performance.

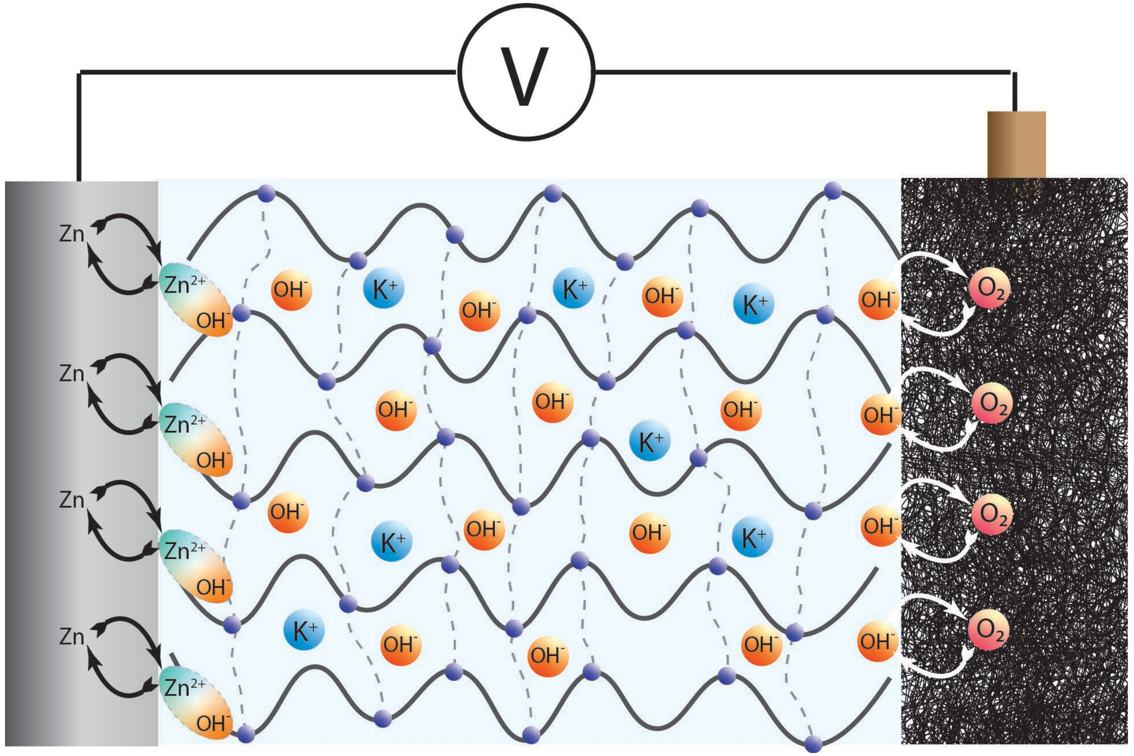
- **Why ORNL:** The lab is uniquely positioned to achieve this goal due to its integrated expertise in materials design and synthesis, electrochemical engineering, and device prototyping.

- **Innovation:** Development of a PGM-free bifunctional catalyst and a novel cross-linked composite polymer membrane that minimizes water loss and maintains high conductivity for long-duration open-air applications.

- **Impact:** If successful, this project will enable affordable, durable, and efficient long-duration energy storage solutions critical for integrating into the electric grid, reducing reliance on scarce and expensive materials, and advancing sustainable energy technologies.

- **Alignment:** This project is aligned with DOE's strategic mission to develop long-duration energy storage system using widely available and critical-component-free materials.

Zinc-Air Cell-Current Challenges & Our Approach



Zn anode | **Gel polymer electrolyte** | **Catalyst embedded carbon/metal foam**

$Zn \leftrightarrow Zn^{2+} + 2e^-$

$4OH^- \leftrightarrow O_2 + 2H_2O + 4e^-$

$Zn^{2+} + 4OH^- \leftrightarrow Zn(OH)_4^{2-}$

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

Anode (Zn metal)

- A homogenous and continuous Zn/Electrolyte interface is desired allowing for efficient Zn plating/stripping

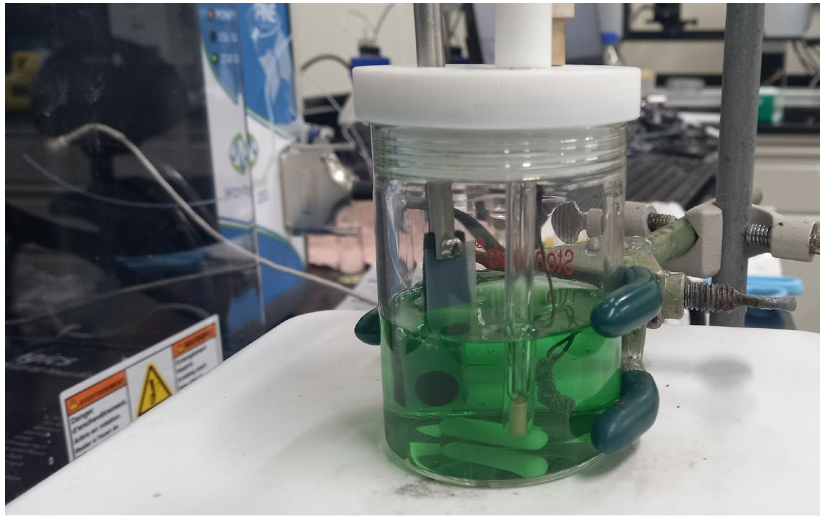
Electrolyte (Gel polymer electrolyte)

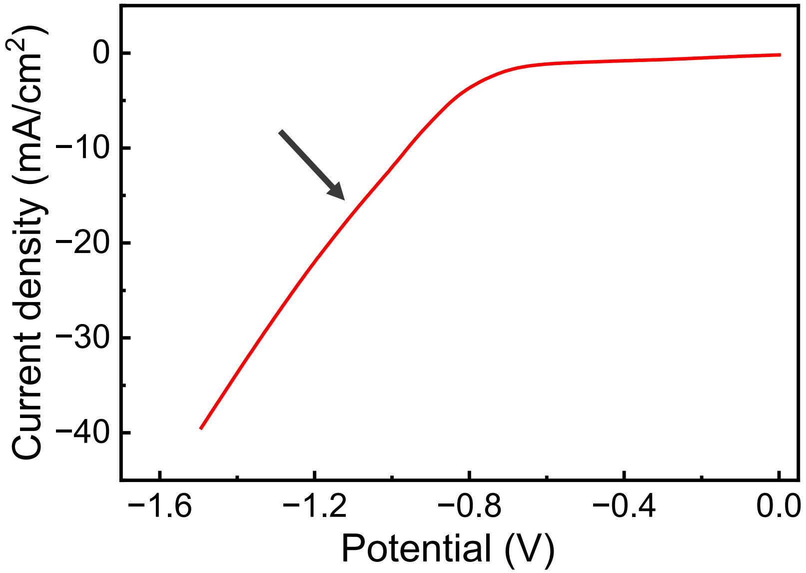
- Enhanced mechanical stretchability
- Highly stable in open atmosphere
- High ionic conductivity
- Excellent water retention ability
- Wide temperature operational window

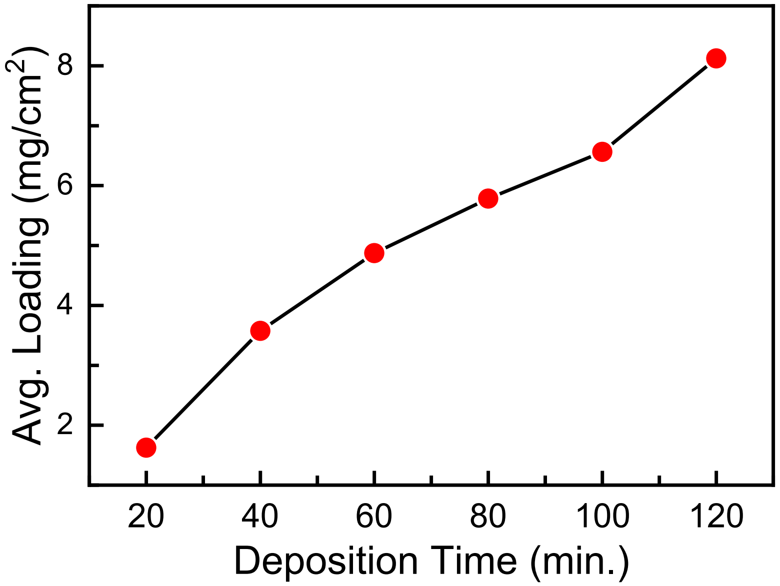
Bifunctional electrocatalyst

- Single catalyst should exhibit both OER and ORR capability
- Stable with operational conditions
- Should exhibit fast interfacial kinetics

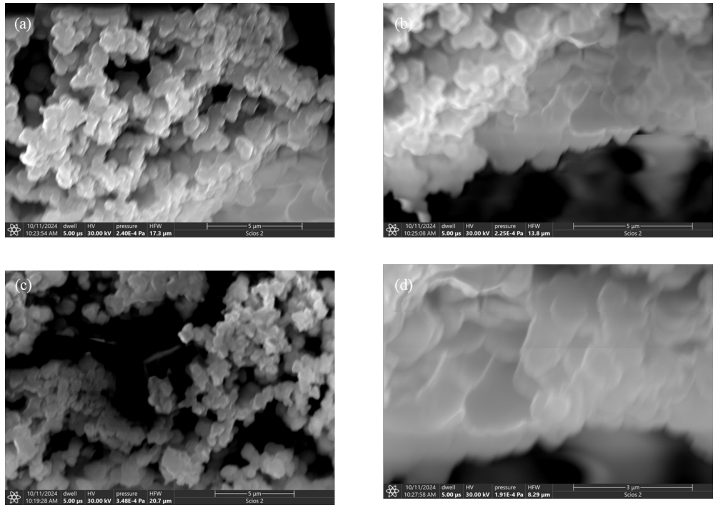
Synthesis and Optimization of M/M’-LDH Electrocatalysts Directly Grown on Current Collectors



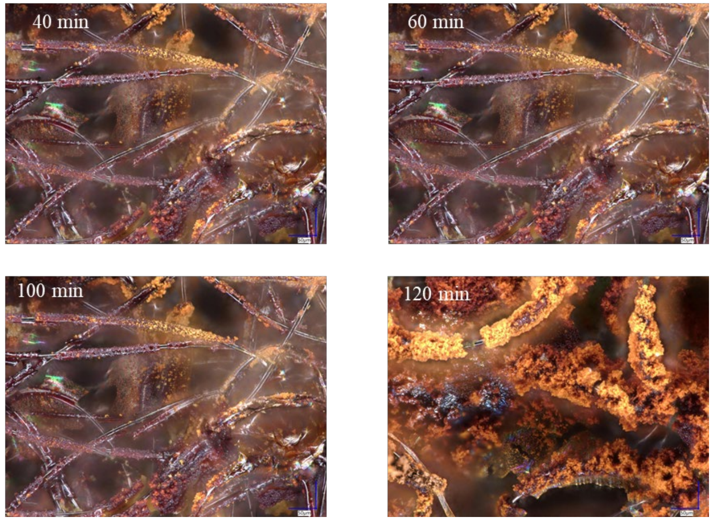




SEM micrograph



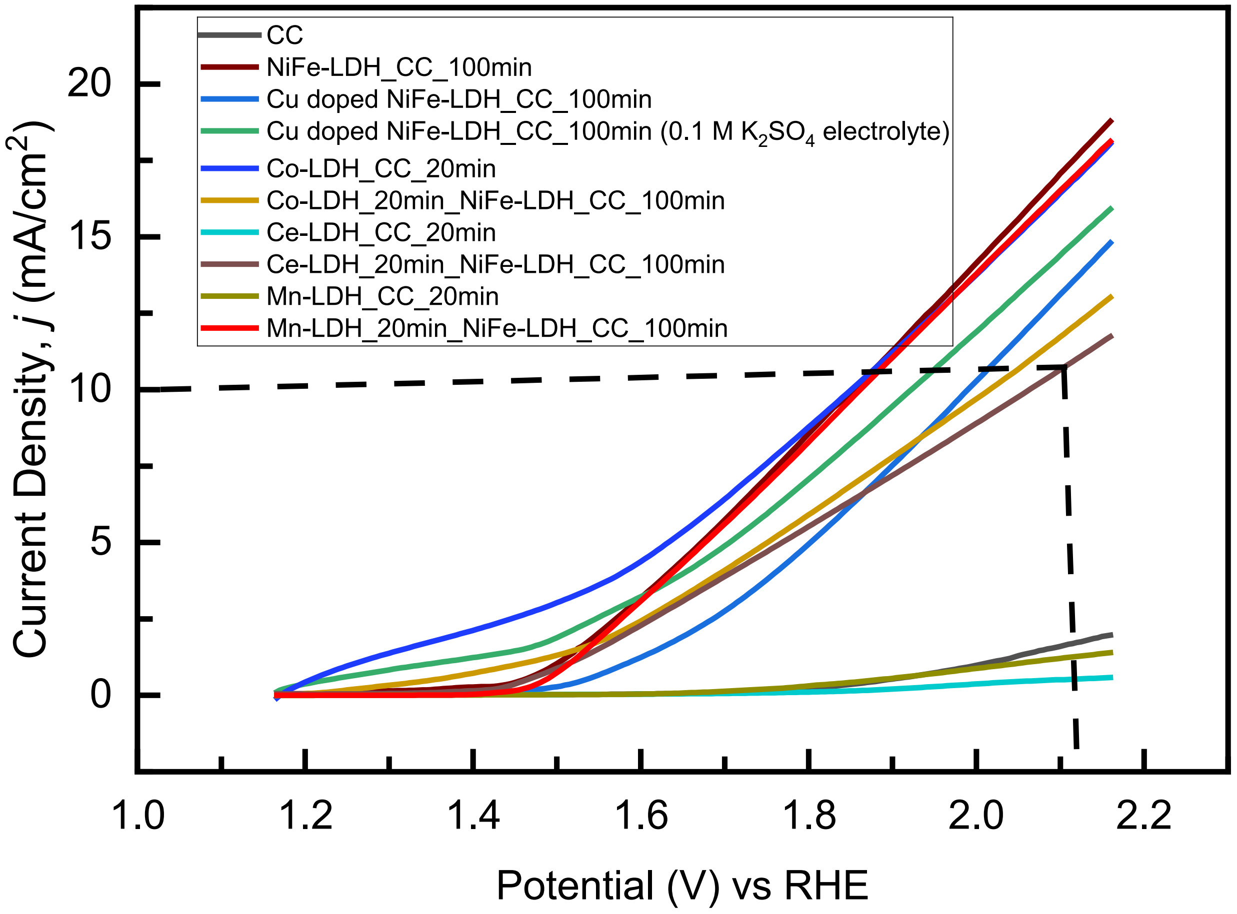
Optical micrograph

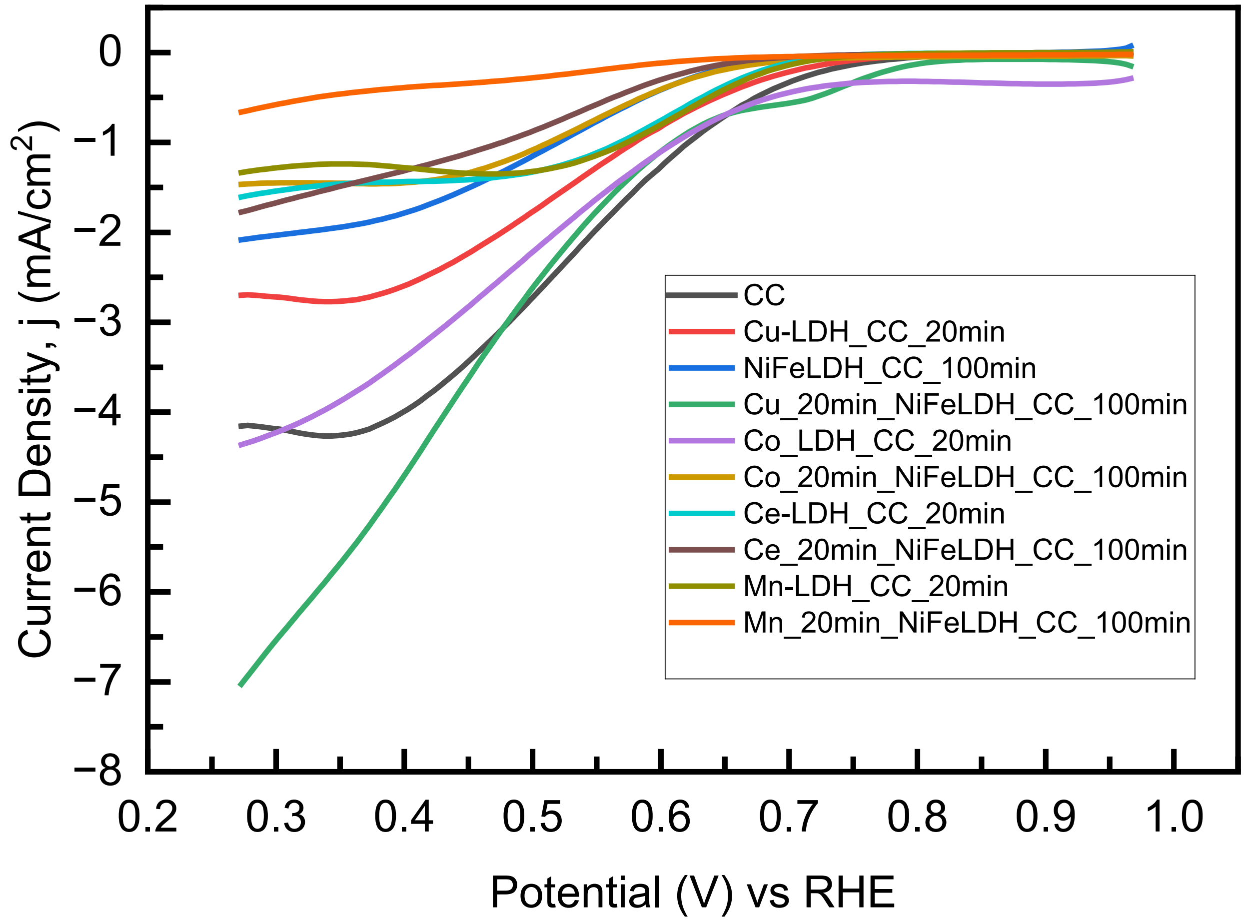


For initial catalyst screening

- Electrochemical synthesis of M1/M2- Layered Double hydroxide catalyst (LDH).
- PGM free materials involved
- Can be easily scaled via CSTR coprecipitation method

Electrochemical Performance of M-M’/LDH Electrocatalyst





Amongst all PGM- free metal catalyst, Ni/Fe- LDH catalyst displays the most promising results with **OER overpotential of 424 mV** and **ORR overpotential of 842 mV** in 0.1 M KOH solution and was selected for further studies.

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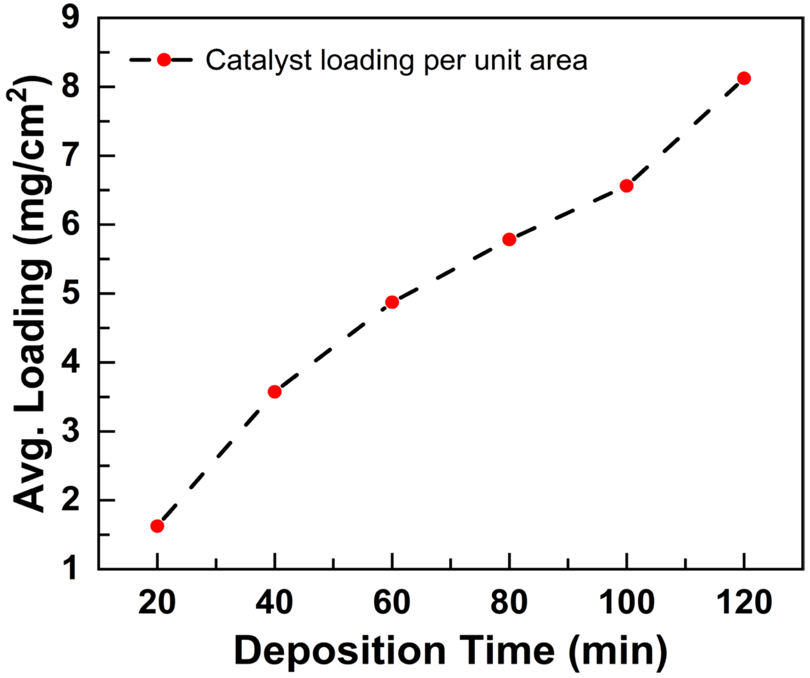
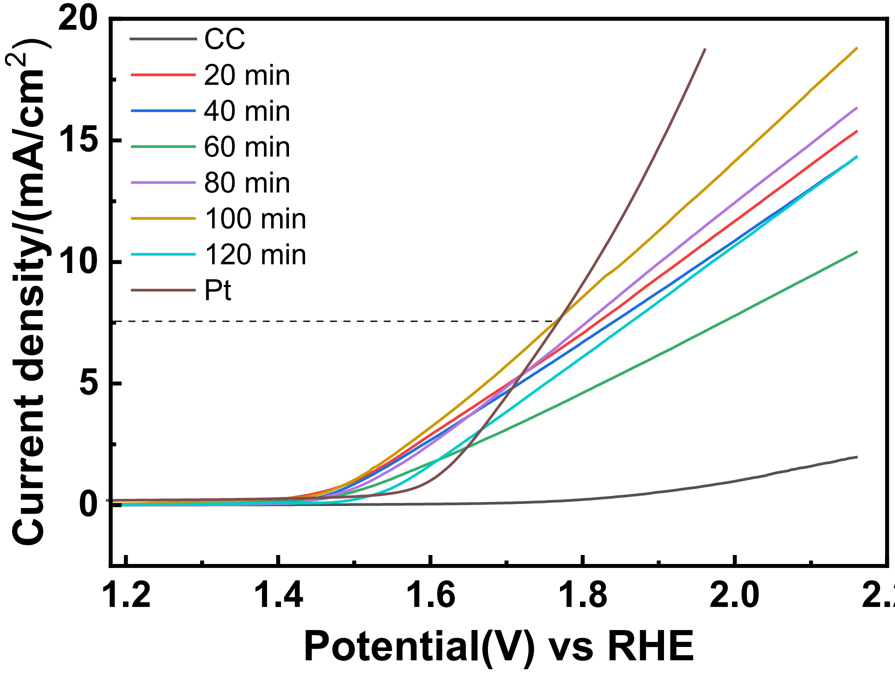
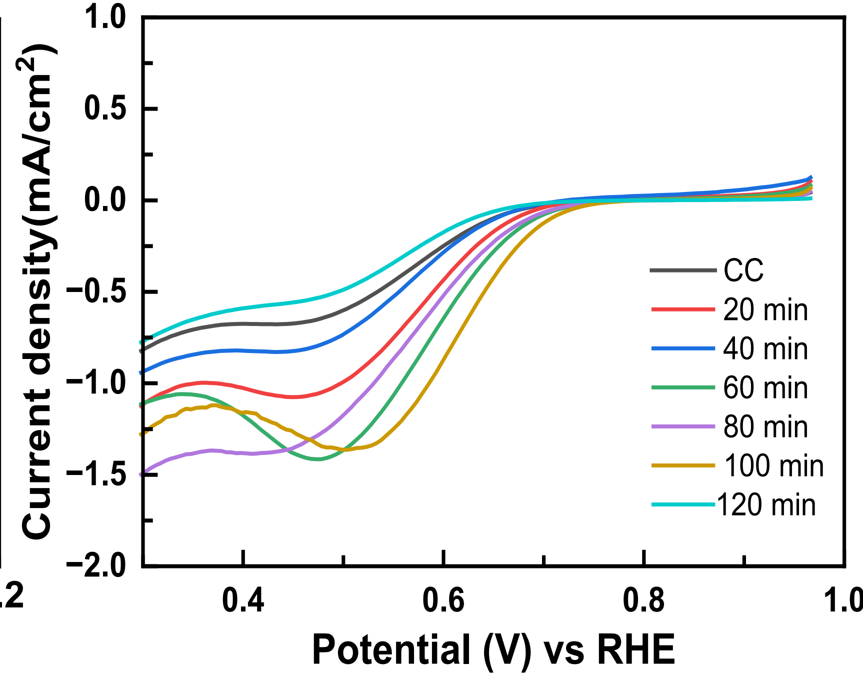
Electrochemical Performance & Optimization of Ni/Fe-LDH Electrocatalyst







Time (min)	Avg. (mg/cm^2)
20	1.624431
40	3.573749
60	4.873294
80	5.782976
100	6.562703
120	8.122157

Time (min)	Overpotential (V)
20	0.674
40	0.738
60	0.903
80	0.673
100	0.624
120	0.739

OER Overpotential

Time (min)	Half-wave Potential, $E_{1/2}$ (V)
20	0.548
40	0.553
60	0.543
80	0.558
100	0.645
120	0.537

ORR Overpotential

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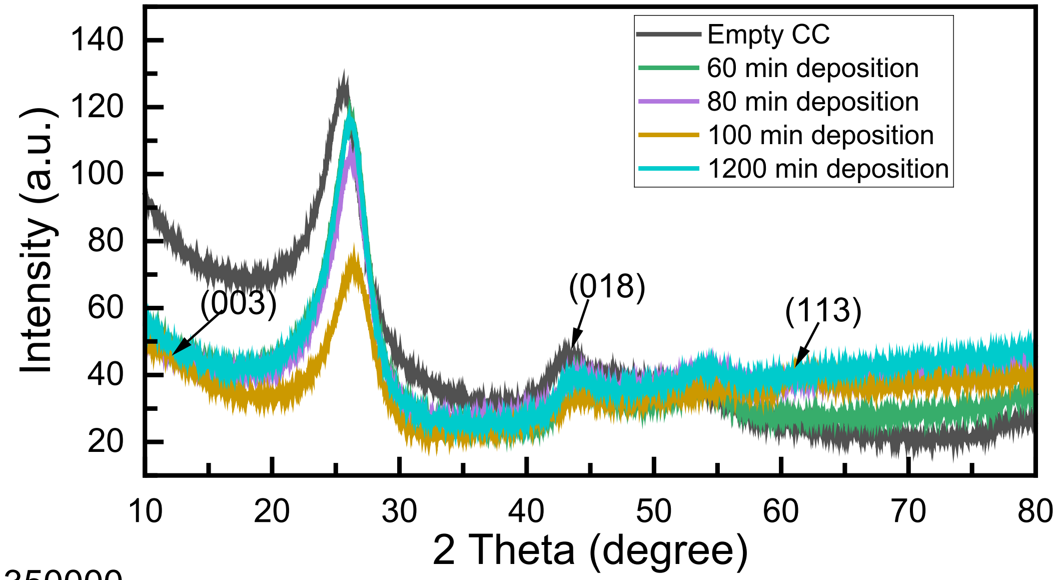
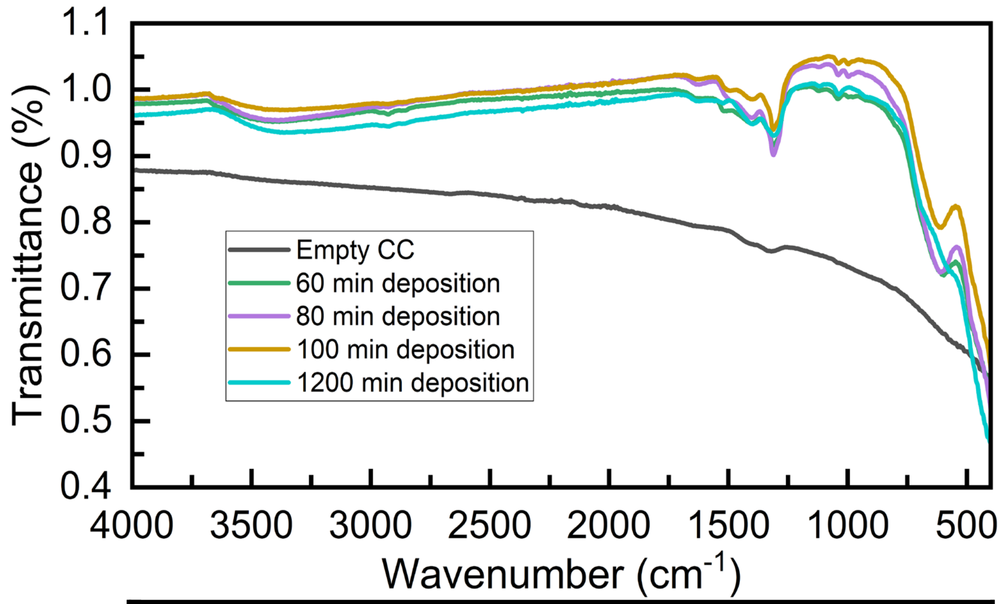
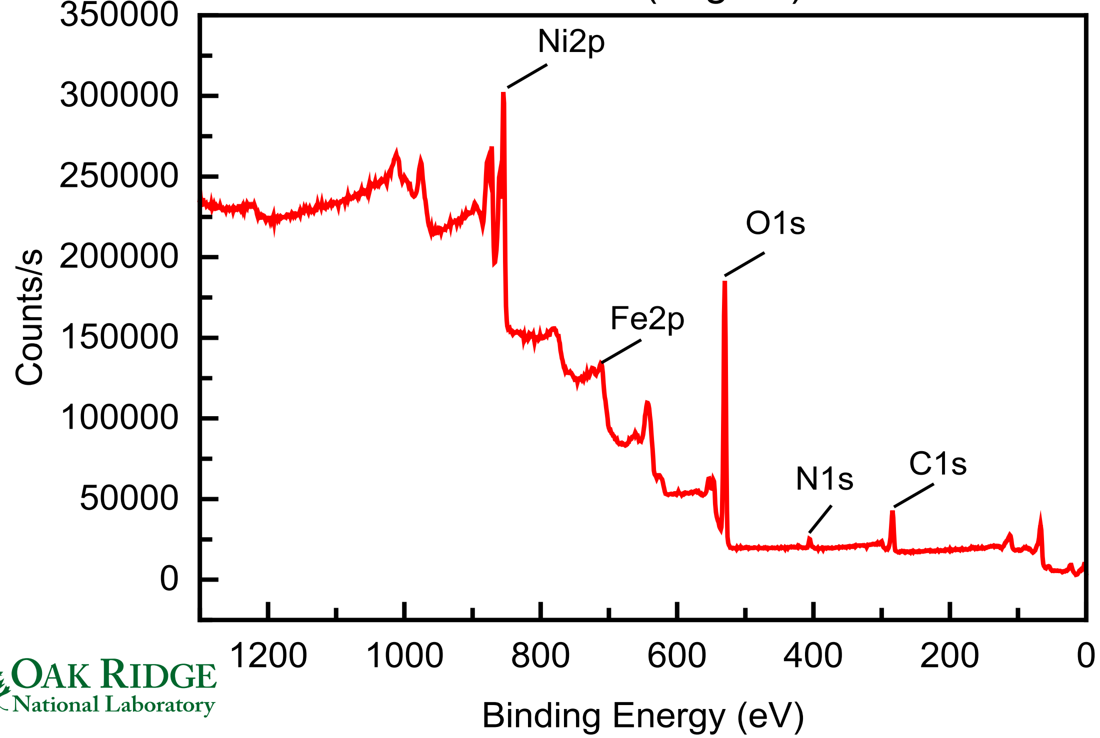
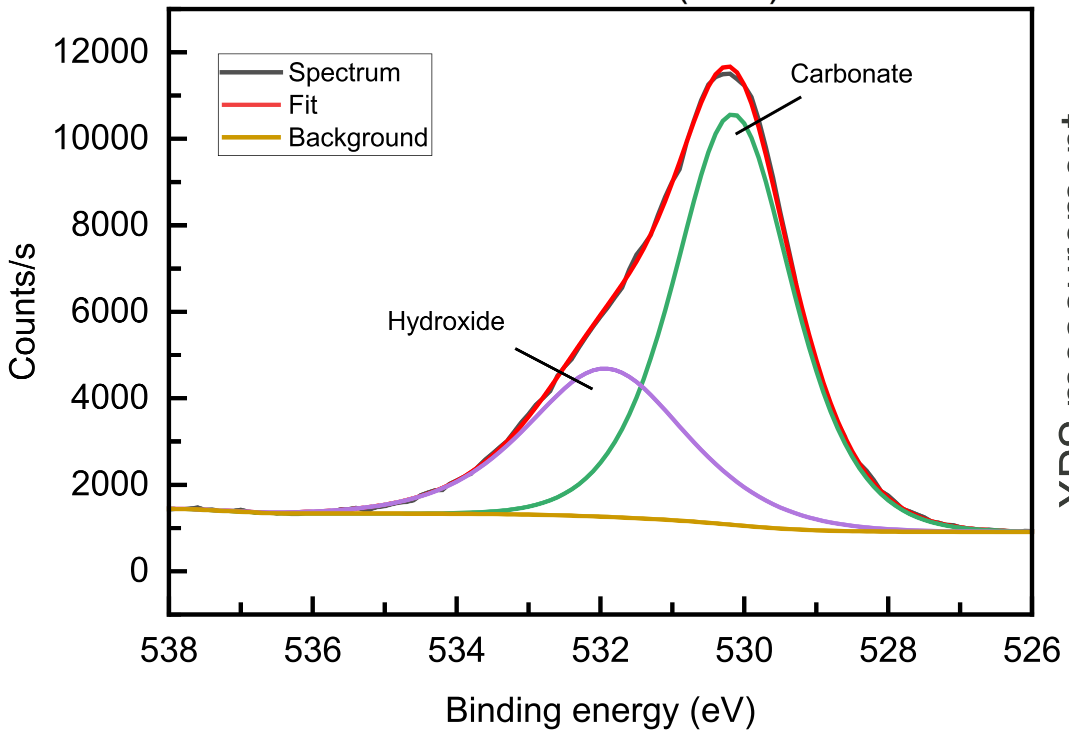
Characterization of Synthesized Ni/Fe-LDH Using XRD, FT-IR, and XPS









XPS measurement estimated the **Ni/Fe ratio: 93.74/6.26**

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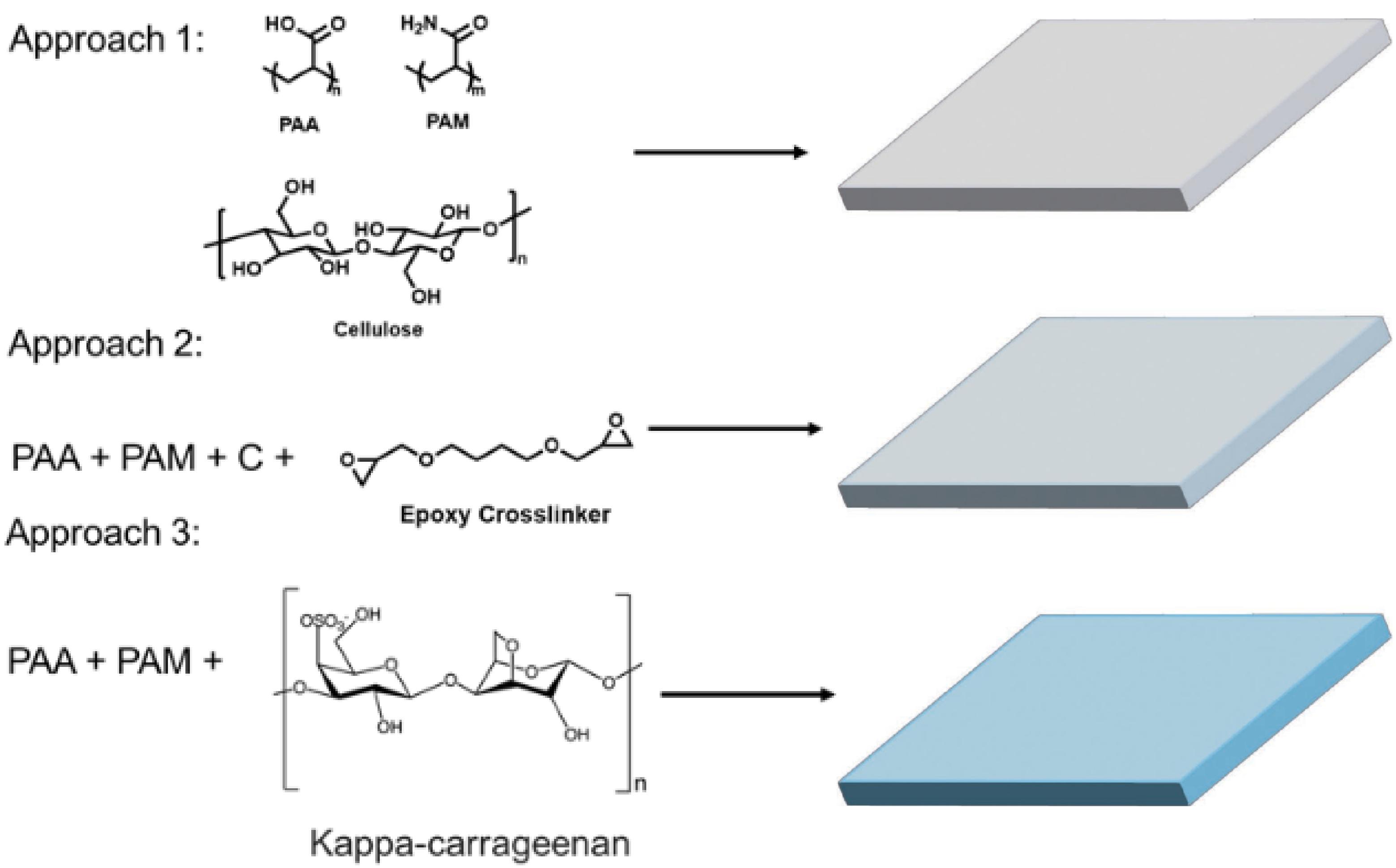
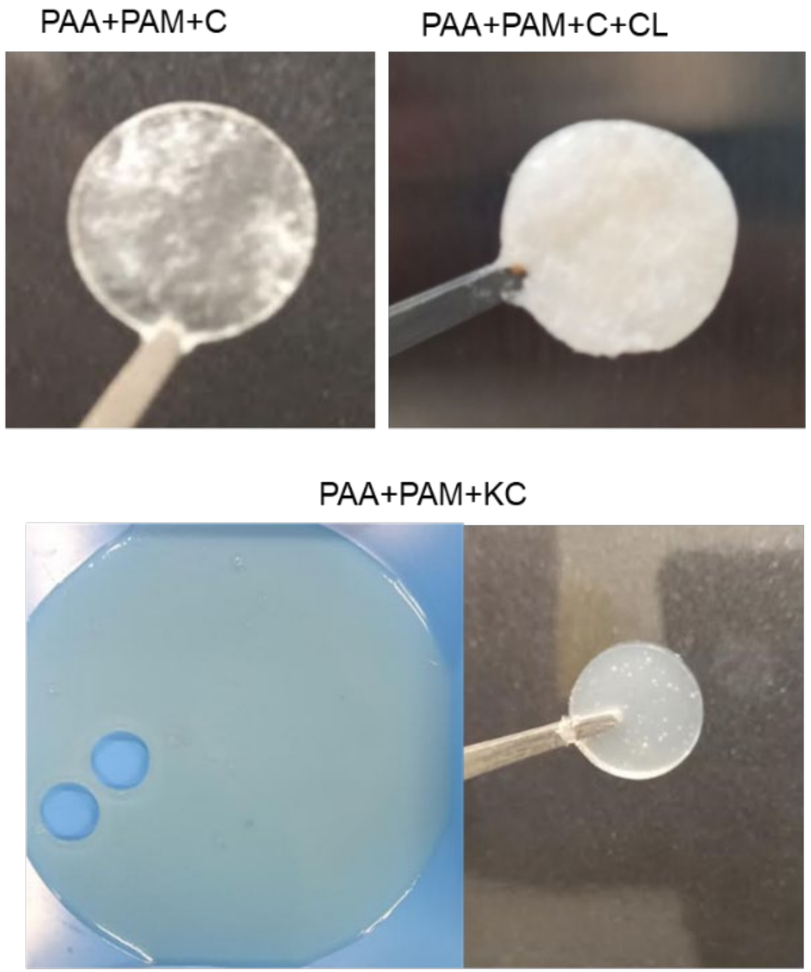
Synthesis and Optimization of Composite Gel Polymer Electrolyte (GPE)

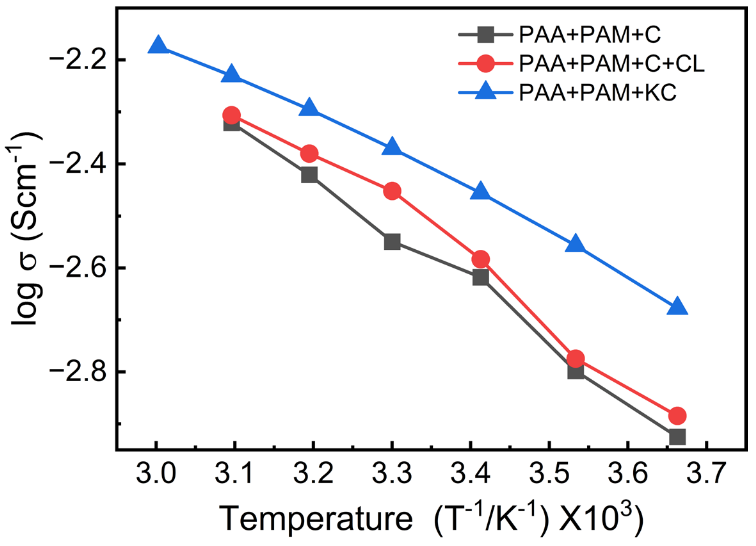
Design and synthesize of gel polymer electrolytes:

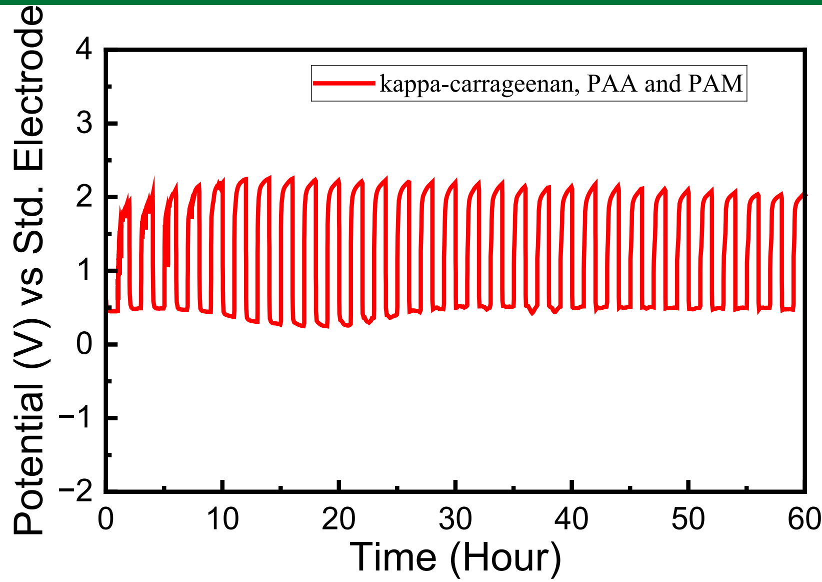


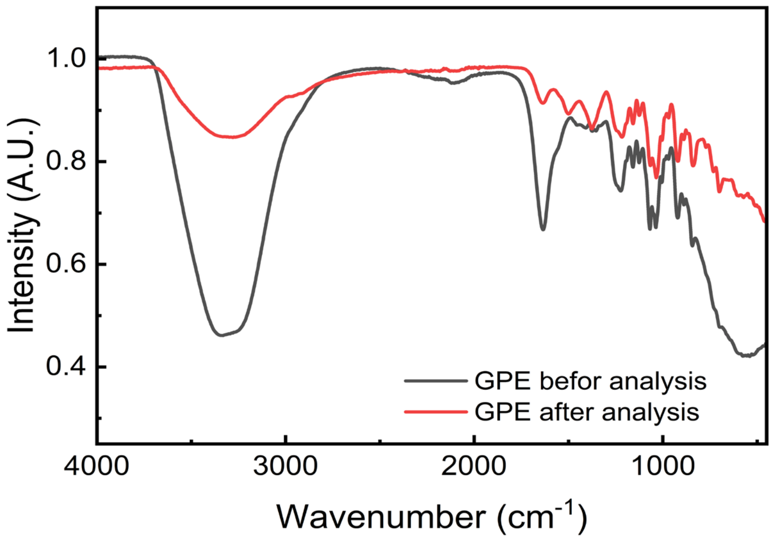


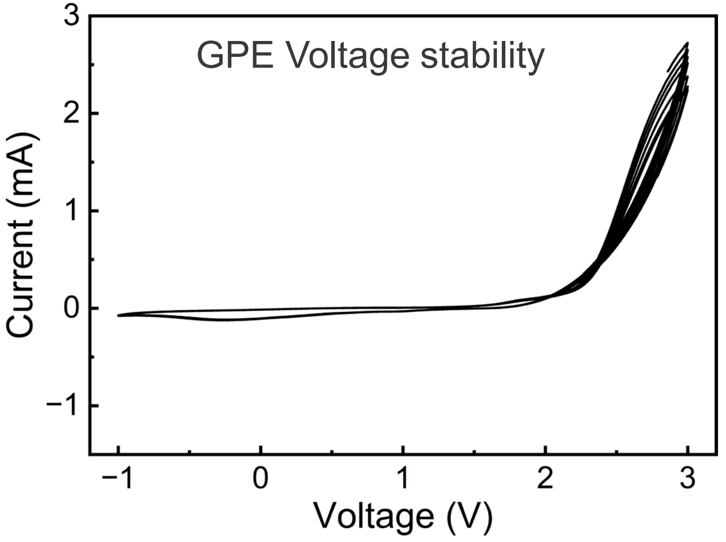
3 different types of PAA and PAM based GPE were fabricated amongst which **PAA+PAM+KC** based GPE displayed maximum water retention

Electrochemical Characterization of Composite Gel Polymer Electrolyte



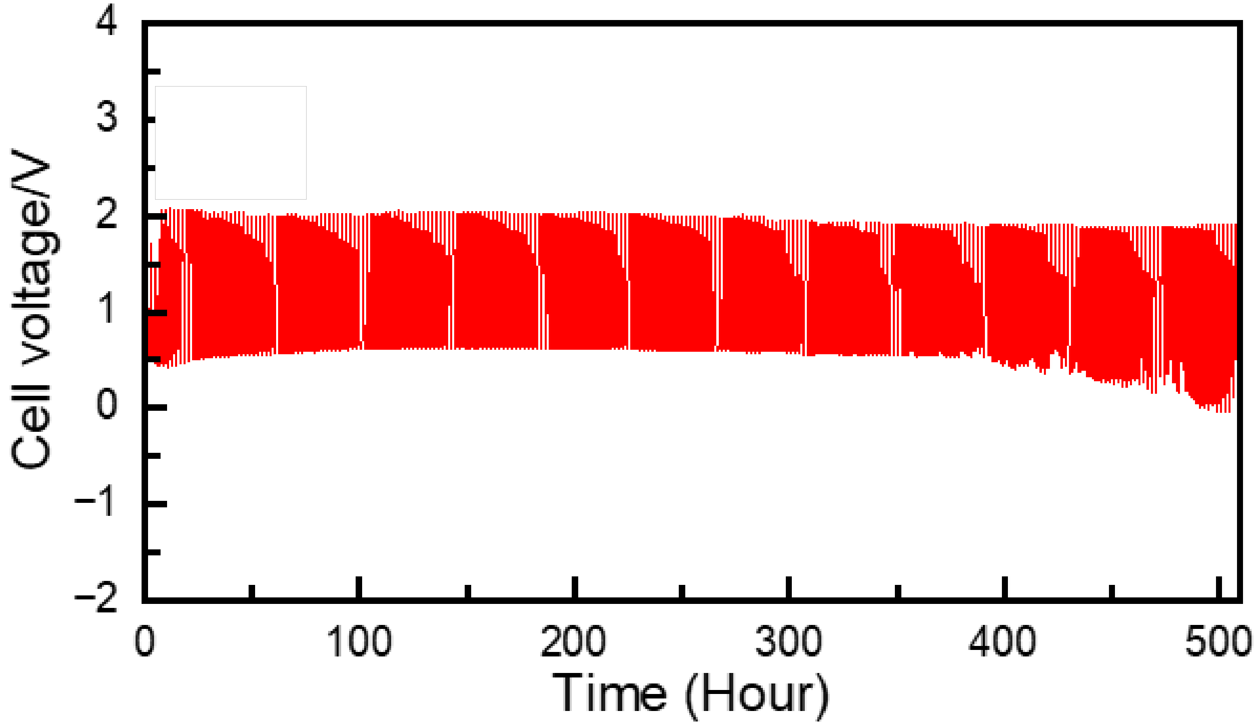




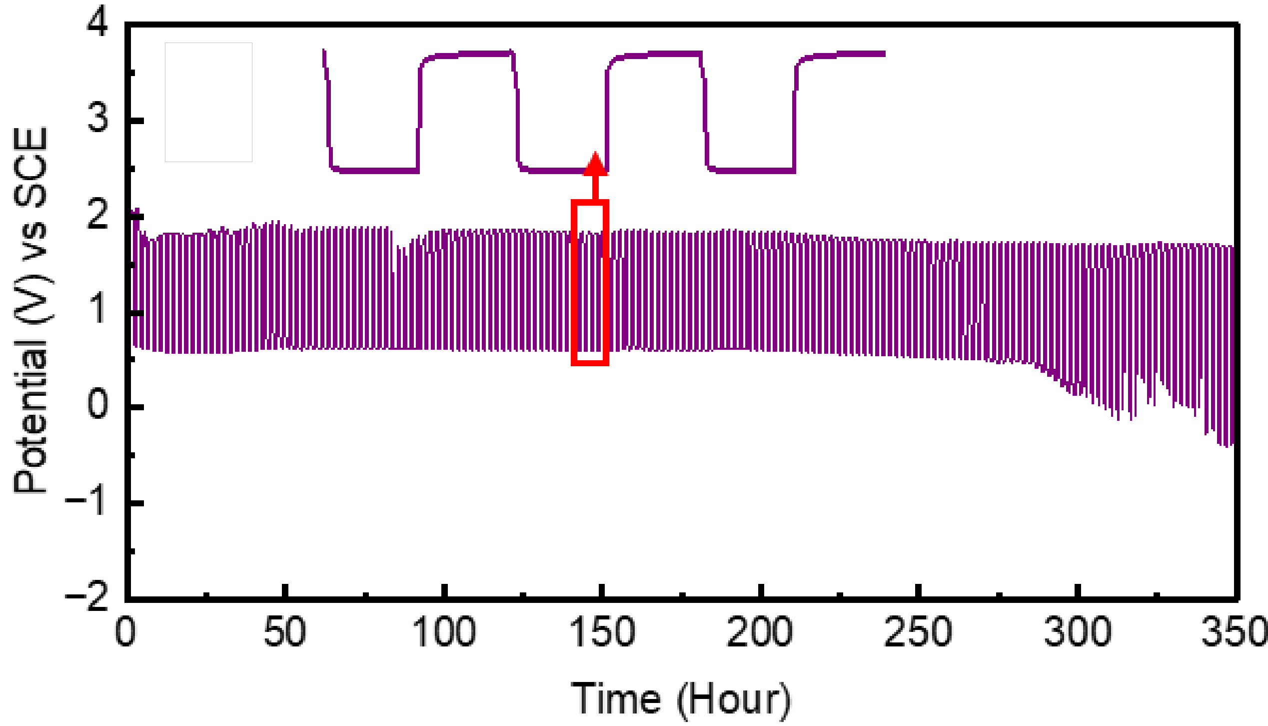


- PAA+PAM+KC based GPE displayed highest ionic conductivity of 6.68 mS/cm at room temperature.
- The PAA+PAM+KC based GPE demonstrated water retention even after hours of cycling in an open-air conditions.
- A voltage stability of ~ 2V was observed, which is within the voltage range of Zinc-air battery.

Cycling Performance of Zn–Air Battery Cells Using PAA/PAM/KC Electrolyte and Ni/Fe-LDH Catalyst Soaked in KOH

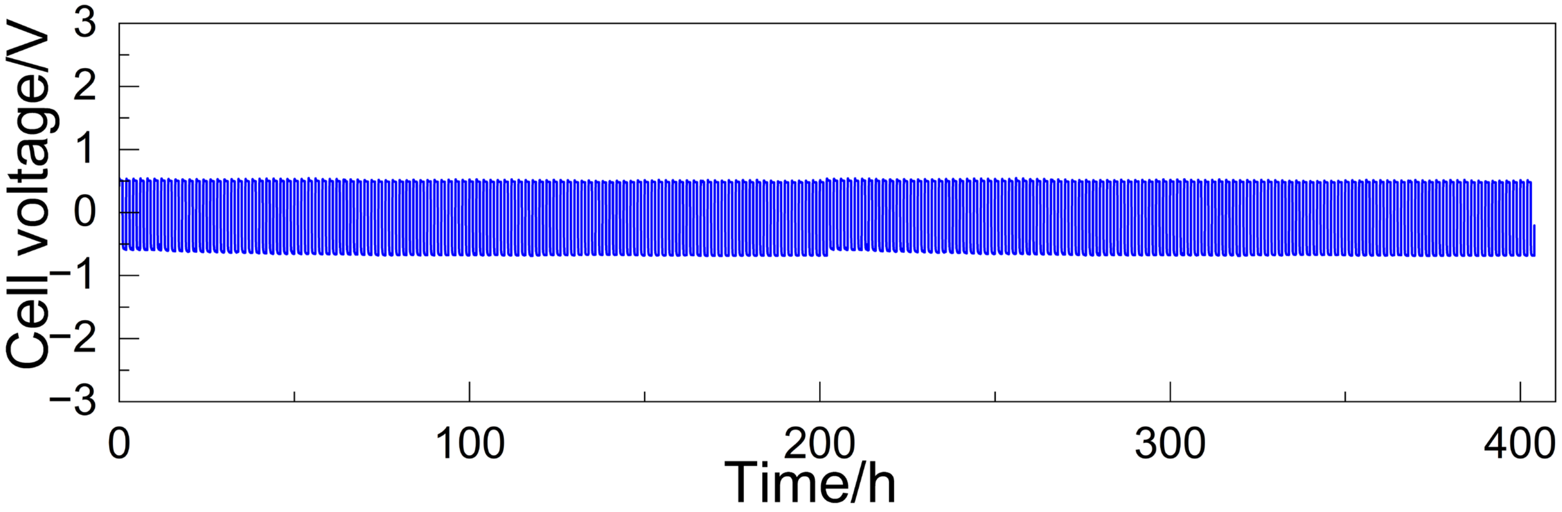


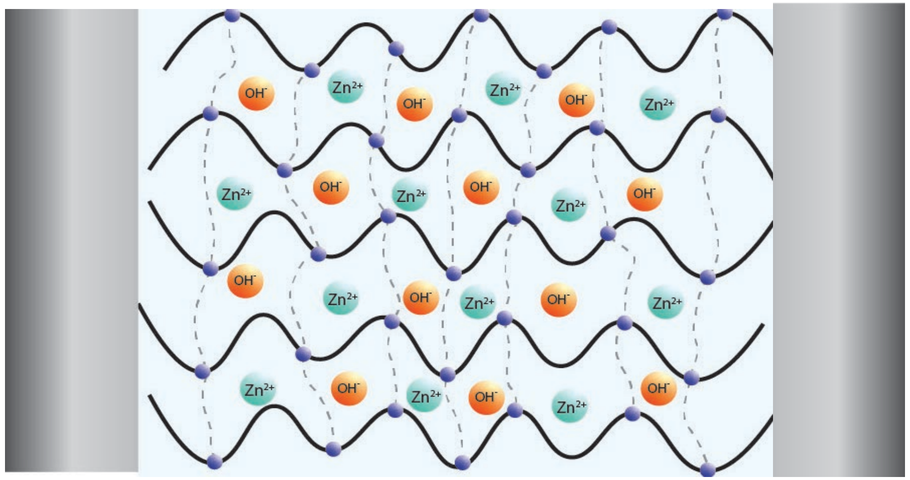
Cyclic stability of Zn-air battery cell under humid condition for over 500 hours

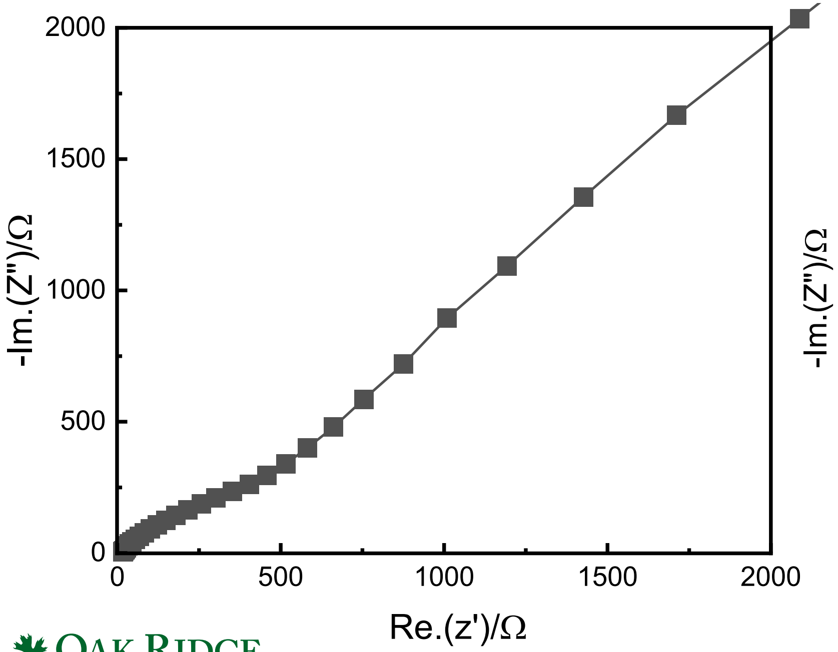


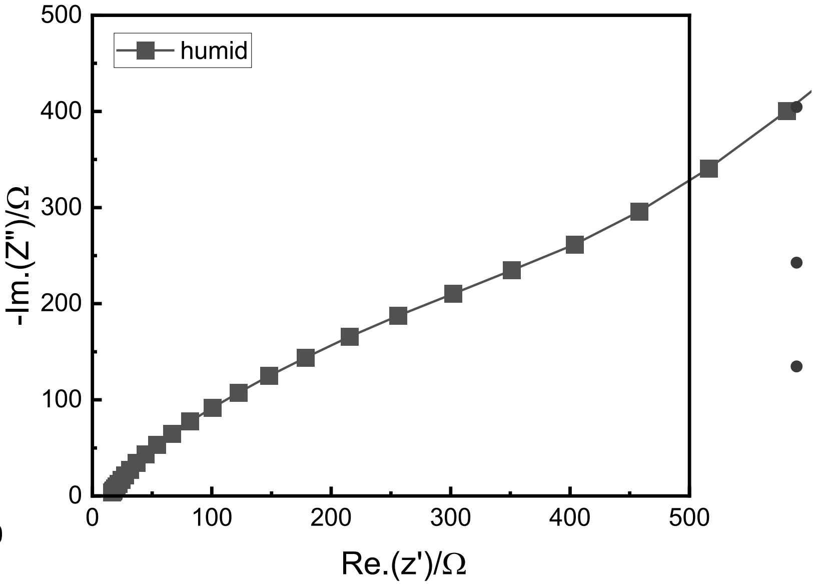
Cyclic stability of Zn-air battery cell under open air condition for over 300 hours

Striping-Plating Behavior of Symmetrical Cell Zn/GPE/Zn Soaked With Zn^{2+} salt





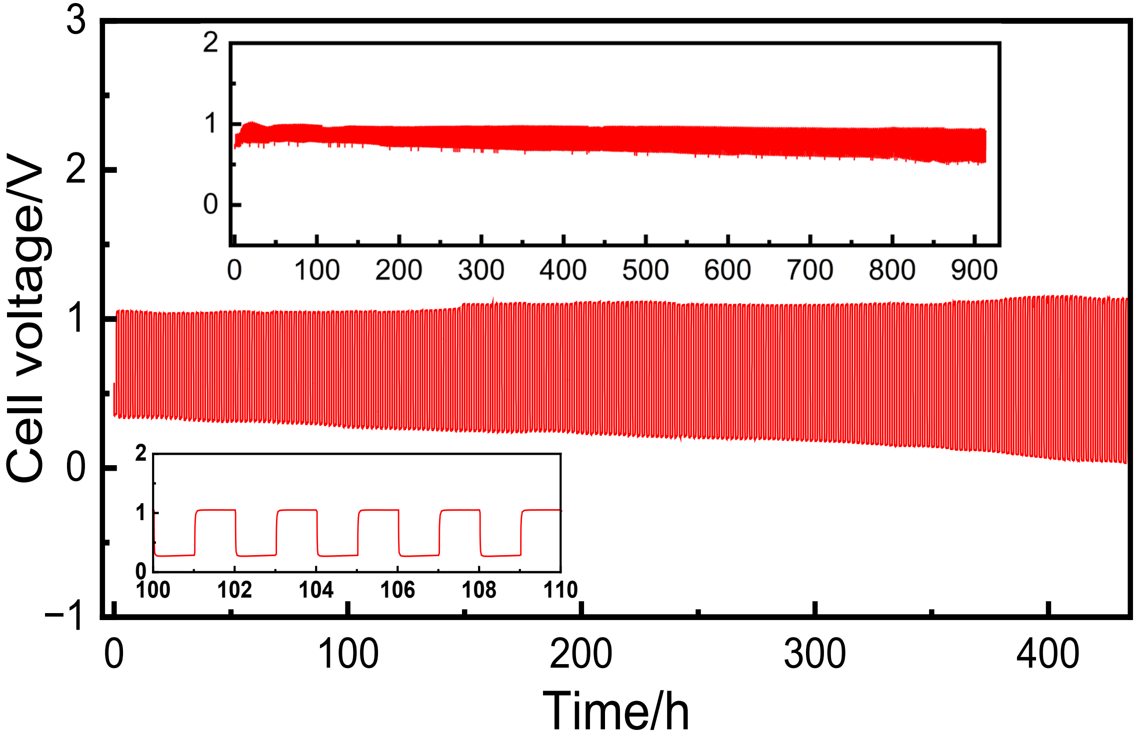




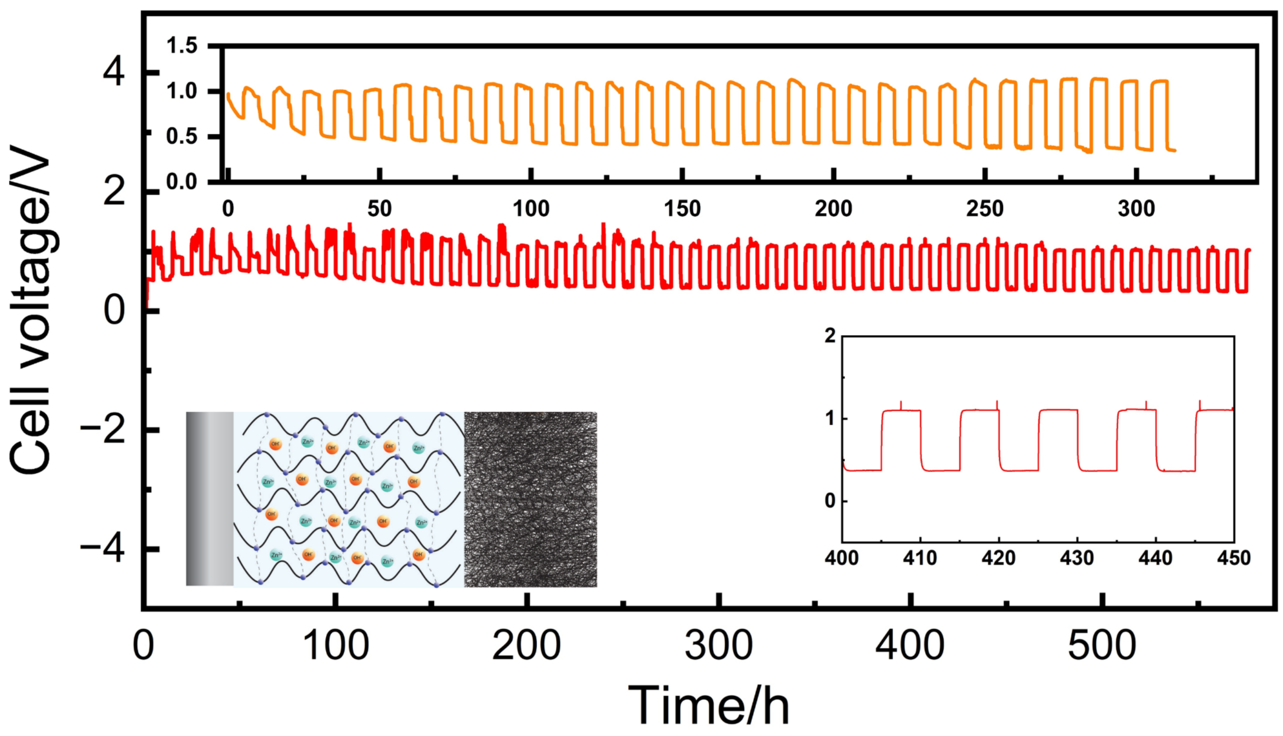
- Homogeneous zinc stripping and plating occurs without the formation of zinc dendrites.
- The cell exhibits relatively high voltage polarization.
- The interfacial resistance is notably elevated.

Cycling Performance of Zn–Air Battery Cells Under Humid Conditions Using $ZnCl_2$-Soaked Polymer Electrolyte Membranes

1h charge and 1h discharge



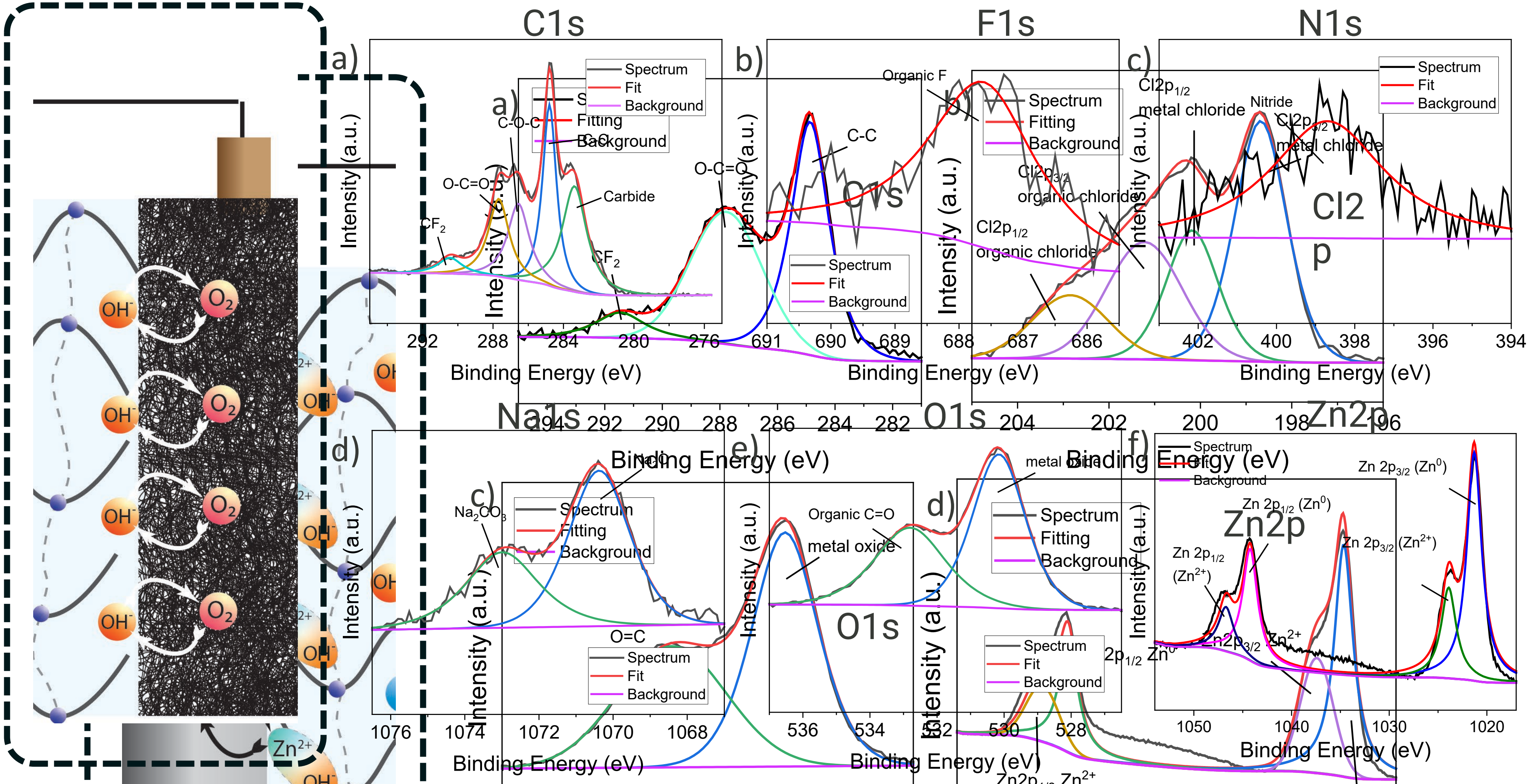
5h charge and 5h discharge



- Cell voltage is less than the equilibrium potential
- Cell polarization gradually increases on cycling

- Theoretical equilibrium potential 1.65 V
- Commonly, the nominal voltage ranges between 1.35 and 1.4V.
- With the voltage under load potentially dropping to as low as 1.2V

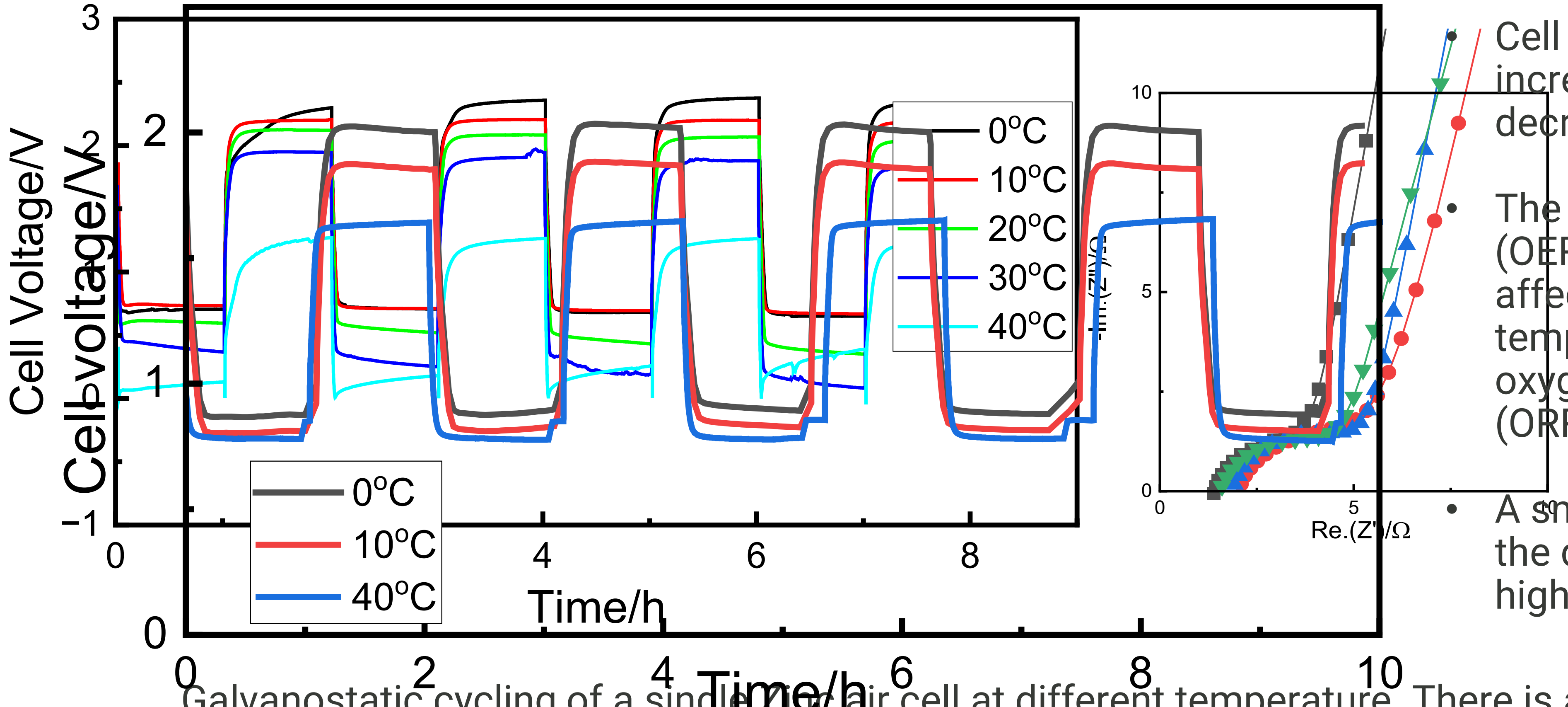
XPS Analysis of Electrolyte–Electrode Interfaces After Cycling

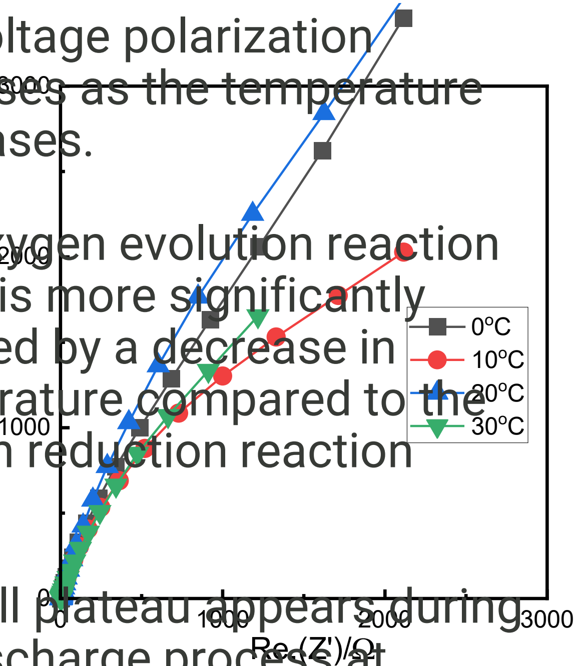


Interestingly, XPS analysis at the cathode interface indicated the presence of Zinc metal, indicating some metal possible metal plating which can be the reason behind lower voltages and possible cell failures.

XPS analysis at the anode interface indicated the presence of expected species such as Cl, Zn.

Cycling Performance of Zn–Air Batteries at Different Temperatures



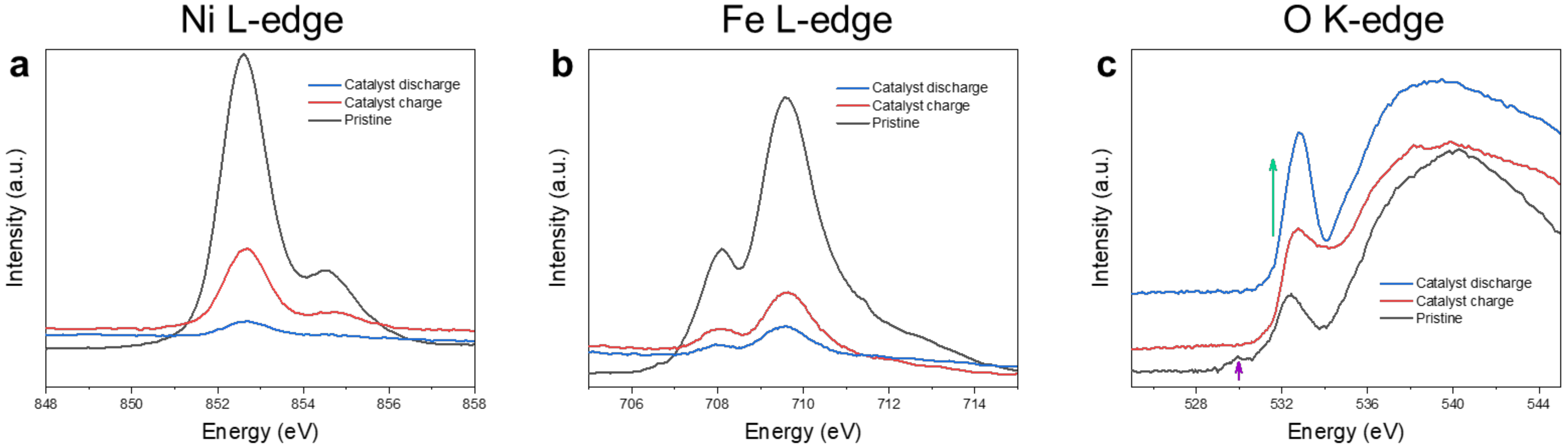


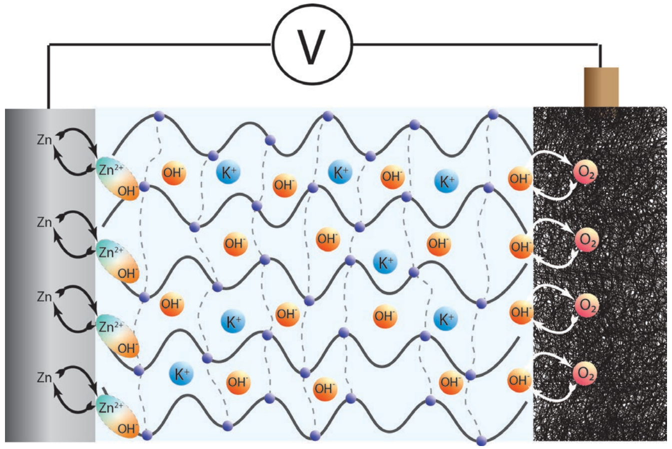
- Cell voltage polarization increases as the temperature decreases.
- The oxygen evolution reaction (OER) is more significantly affected by a decrease in temperature compared to the oxygen reduction reaction (ORR).
- A small plateau appears during the discharge process at higher temperatures.

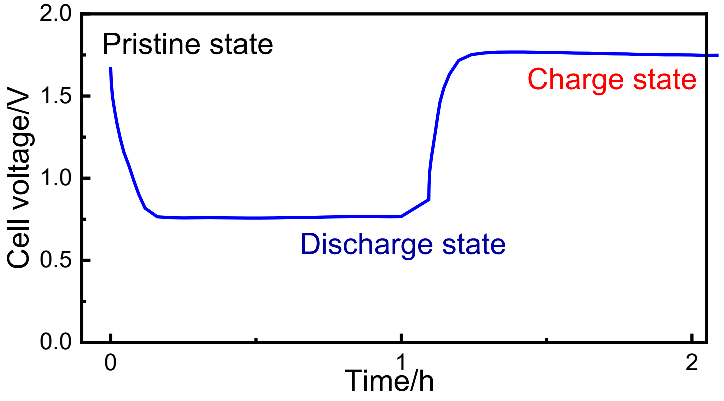
Galvanostatic cycling of a single Zinc air cell at different temperature. There is a big increase in ORR overpotential with decreasing temperature. The increase in OER with increasing temperature is rather surprising and needs to be studied further

Galvanostatic cycling of 3 different Zinc air cell at different temperature.

Investigation of Catalytic Properties Using Soft X-ray Absorption Spectroscopy (XAS) in Total Electron Yield (TEY) Mode







- Ni and Fe L3-edge spectra at the pristine state indicate 2^+ and 3^+ oxidation states, respectively.
- The oxidation states of Ni and Fe does not change upon cycling as the relative peak intensities of the L3-edges remains mostly the same.
- lower peak intensity upon cycling indicates that the concentration of Ni and Fe is reduced within the probing depth of the TEY mode.
- O K-edge spectra point towards a direct participation of oxygen species on the catalyst towards oxygen redox reaction.

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Summary and Plan for Upcoming Technical Approaches

- **KC Based gel polymer electrolyte exhibits superior performance owing to its better water retention capability.**
  - Optimization of GPE is needed to further enhance the performance in ambient conditions and at wide temperature range.

- **$Ni_xFe_\gamma(OH)_2$ catalyst shows decent performance but further optimization of catalyst is required to decrease the cell overpotential.**
  - Composite multi-catalyst approach will be investigated. For example, Fe-N-C based catalyst will be employed with NiF-LDH to for increasing the ORR activity.

- **XPS analysis of Carbon cathode revels presence of metallic zinc, indicating the formation of zinc dendrites.**
  - Alloyed Zinc anode or electrodeposited anode will be investigated to mitigate dendrites.

Scientific Artifacts

- R. Amin *et al.*, *J. Mater. Chem. A*, DOI: 10.1039/d4ta01061b). It has been selected by Editors as a ***Journal of Materials Chemistry A* Hot Article, 2024**.
- M. Rahman---- R. Amin *et al.*, *Electrochemical Energy Review*, DOI: 10.1007/s41918-025-00249-w, 2025.
- M. Rahman---- R. Amin *et al.*, POWER-D-25-03349) title: “Composite Biopolymer Electrolytes for High-Performance Reversible Zinc-Air Batteries”, under review.
- One manuscript is almost ready to be submitted, and another manuscript is under preparation.
- Oral presentation given at MRS fall meeting in Boston, 2024.
- One poster was presented in the OE annual review meeting in Seattle, 2024.
- Abstract is accepted for oral presentation in the electrochemical Society Meeting in Chicago, 2025 entitled: "Impact of Catalyst Morphologies and Superionic Conductivity of Gel Polymer Electrolyte for Long Duration Reversible Zn-Air Battery”
- PI is one of the symposium organizers and is invited to chair the several sessions of ECS PRiME meeting 2024 in Honolulu, Hawaii.

ACKNOWLEDGEMENTS

- This research was carried out at Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the US Department of Energy (DOE) under contract DE-AC05-00OR22725
- This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division.
- We would also like to thank Program Manager Caitlin A. Callaghan for her valuable suggestions and guidance throughout the project.