Stabilizing Zn Anodes by Molecular Interface Engineering with Amphiphilic Triblock Copolymer

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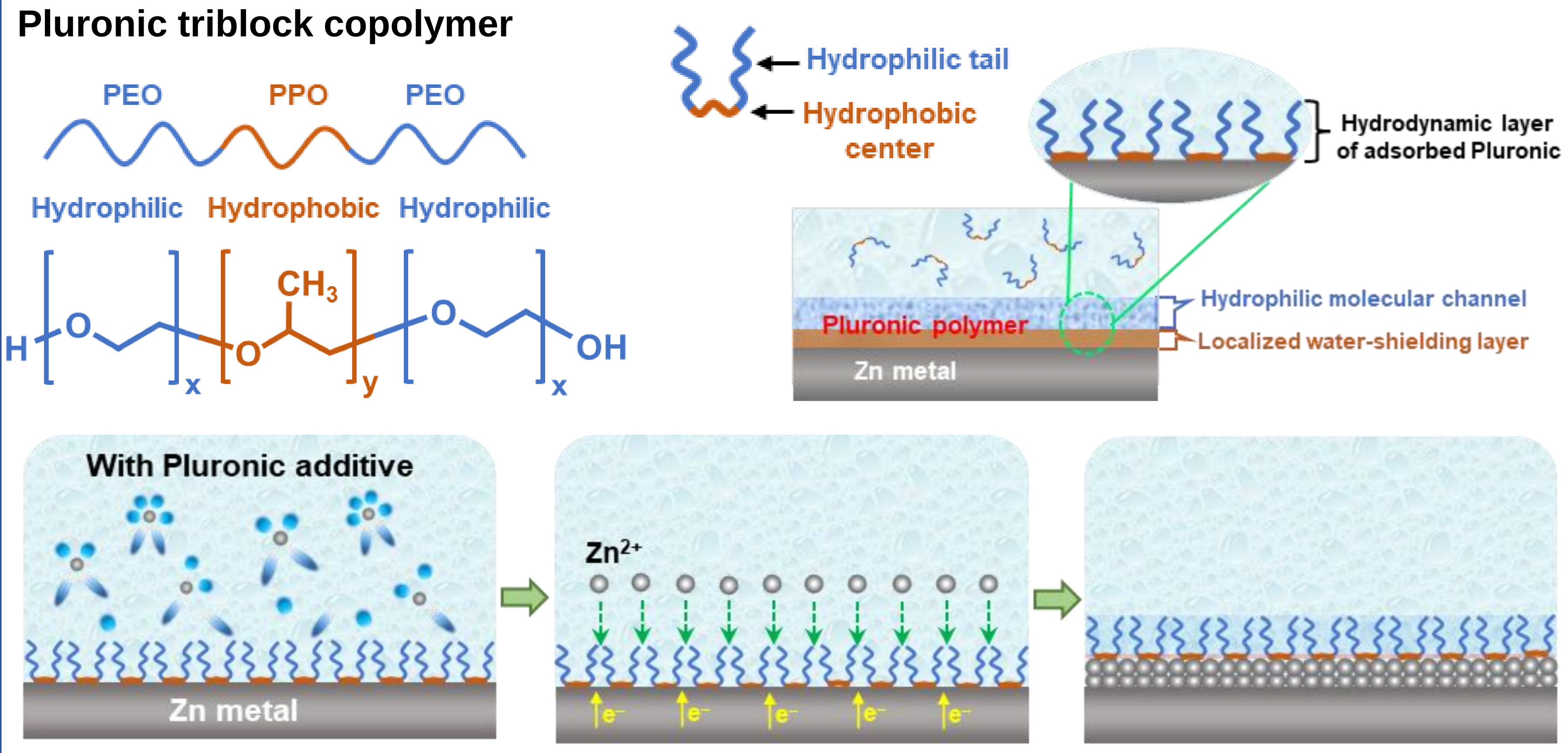
Introduction

Aqueous Zn-based electrochemical technologies hold promise for large-scale energy storage applications, yet challenges persist in the unsatisfied Zn reversibility arising from an unstable Zn anode/electrolyte interface. Therefore, optimizing the Zn/electrolyte interface is of great significance in improving the reversibility of Zn anodes. Introducing functional electrolyte additives has shown promise in stabilizing interfacial reactions. Creating a dynamically stable interfacial environment that can regulate the hydrophobicity of the Zn anode/electrolyte interface is crucial to designing functional electrolyte additives.

- Amphiphilic Pluronic triblock copolymers featuring hydrophobic poly(propylene oxide) (PPO) and hydrophilic poly(ethylene oxide) (PEO) segments are proposed as a new class of electrolyte additives to develop a functionally stable Zn anode interface
- Pluronic additives are beneficial for constructing a hydrodynamic interphase, where the hydrophobic PPO center shields the Zn surface from water-induced side reactions and PEO side blocks guide the homogeneous Zn^{2+} redistribution.

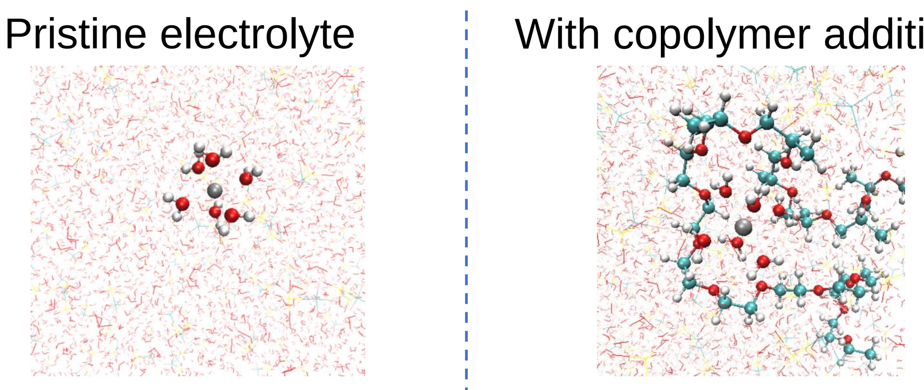
Approach and Objective



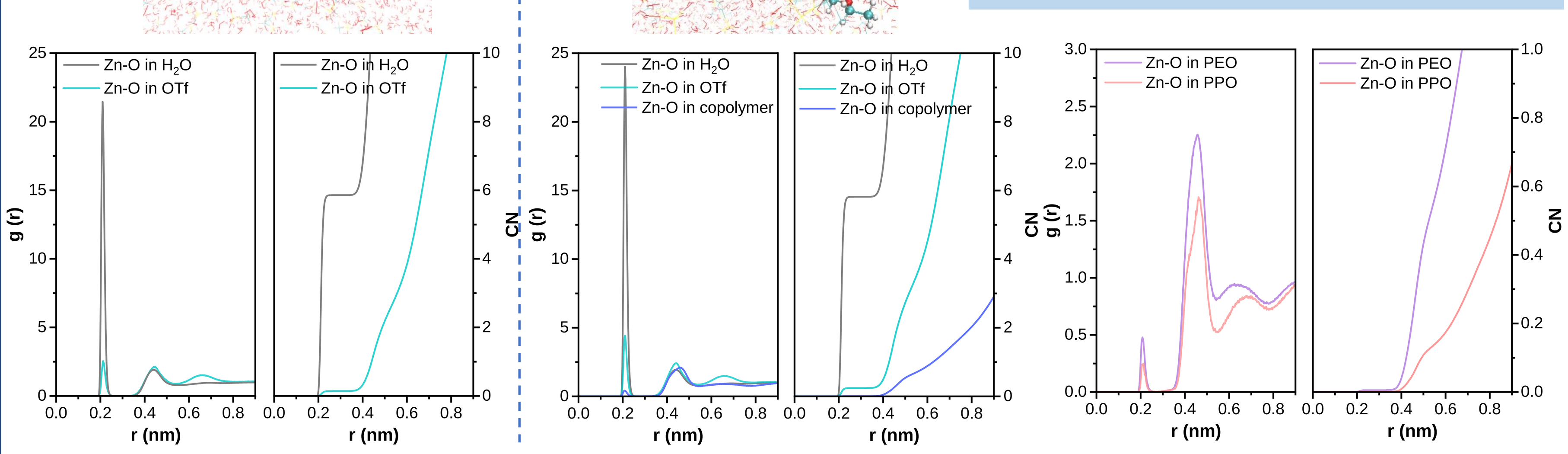
- Stable Zn/electrolyte interface
- Smooth Zn^{2+} ions migration
- Uniform Zn deposition
- Reversible Zn plating/stripping

Simulation results

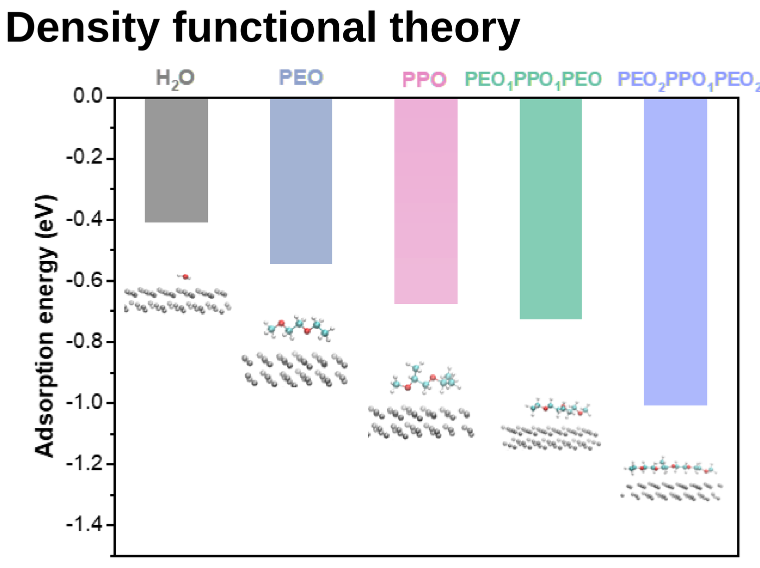
Molecular dynamics



- Polymer exists in the outer solvation sheath of Zn^{2+}
- A relatively stronger interaction between Zn^{2+} and PEO



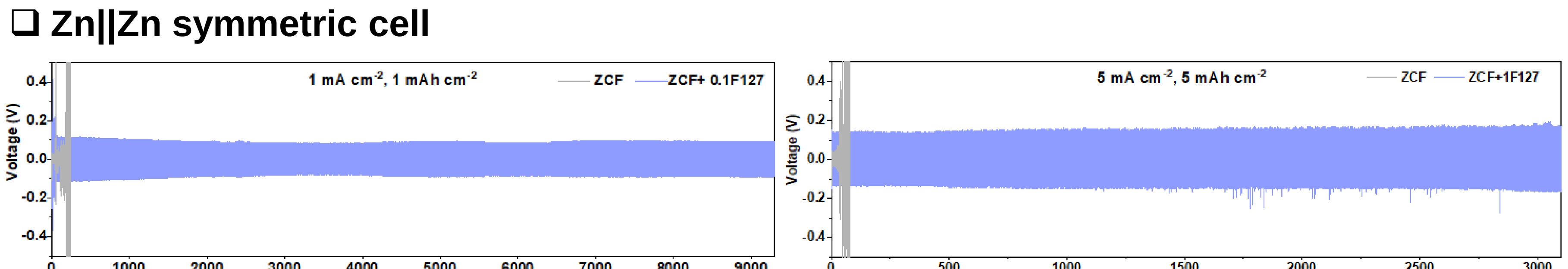
Density functional theory



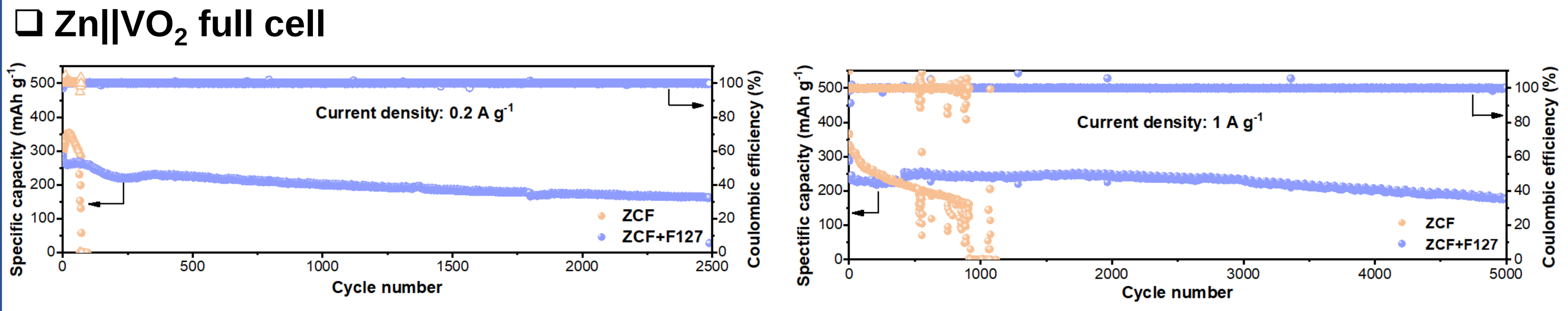
- Copolymer exhibits strong affinity for the Zn metal surface.
- The preference of hydrophobic PPO segments within the Pluronic polymer adsorbed onto the Zn metal surface.

Electrochemical performance

Zn||Zn symmetric cell



Zn||VO_2 full cell

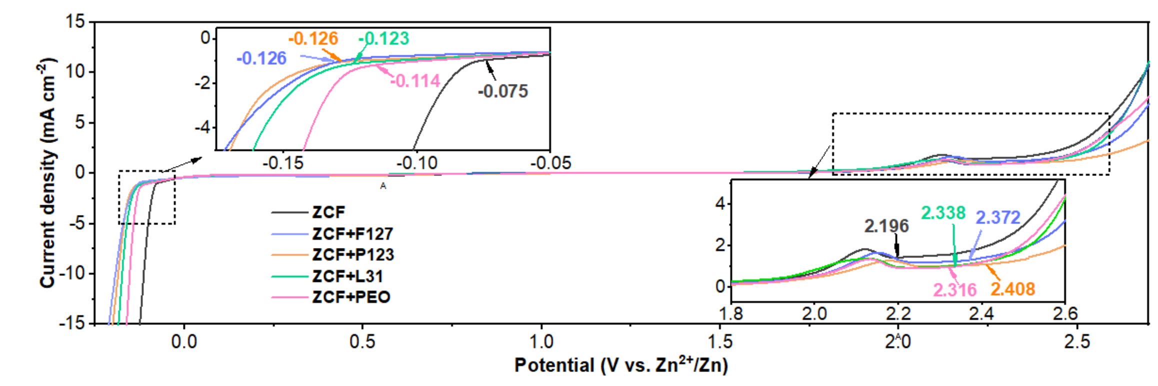


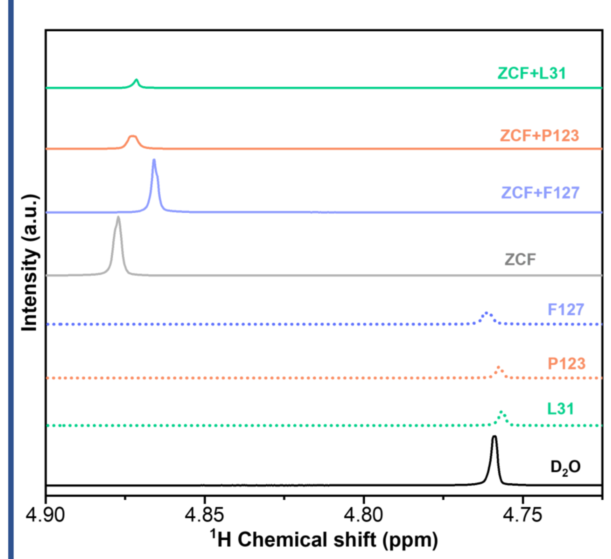
The superior cyclability demonstrated the effectiveness of the F127 additive in stabilizing the Zn anode.

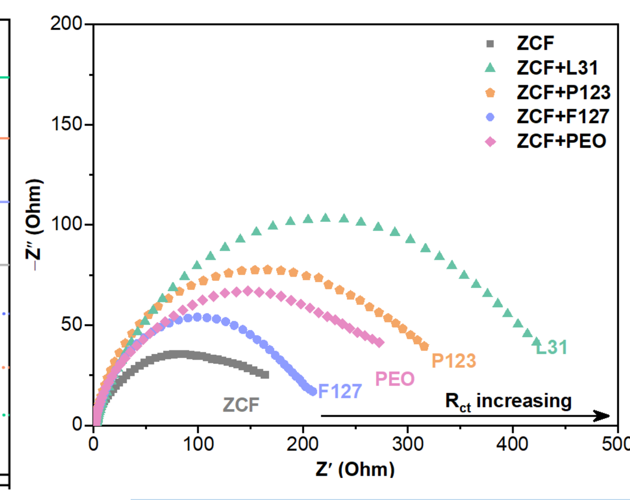
Optimizing electrolyte formulation

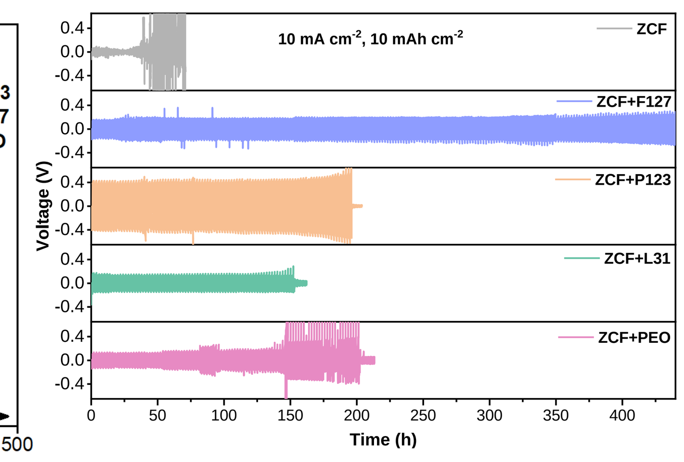
Additive candidates

Polymer	Molecular composition	% EO	Molecular weight
F127	$EO_{100}PO_{70}EO_{100}$	70	12,600
P123	$EO_{20}PO_{70}EO_{20}$	30	5800
L31	$EO_2PO_{18}EO_2$	10	1000
PEO	$(-CH_2CH_2O-)_n$	100	100,000





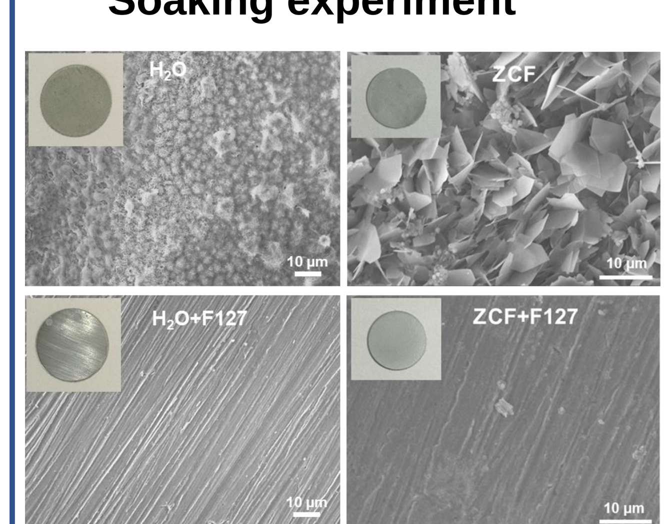




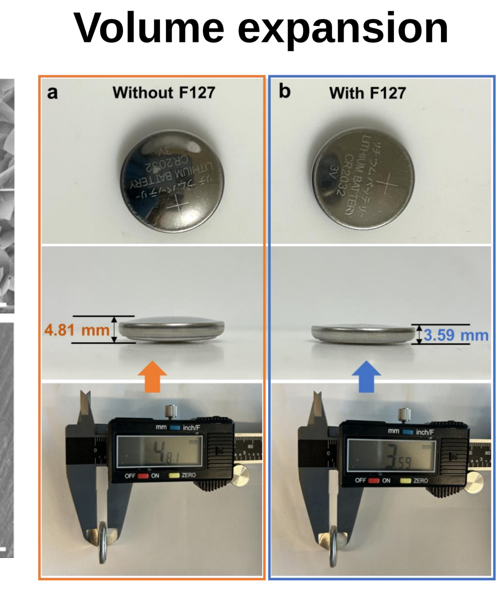
Pluronic F127 is demonstrated as a promising additive for regulating the Zn/electrolyte interface

Suppressing side reactions and zinc dendrite growth

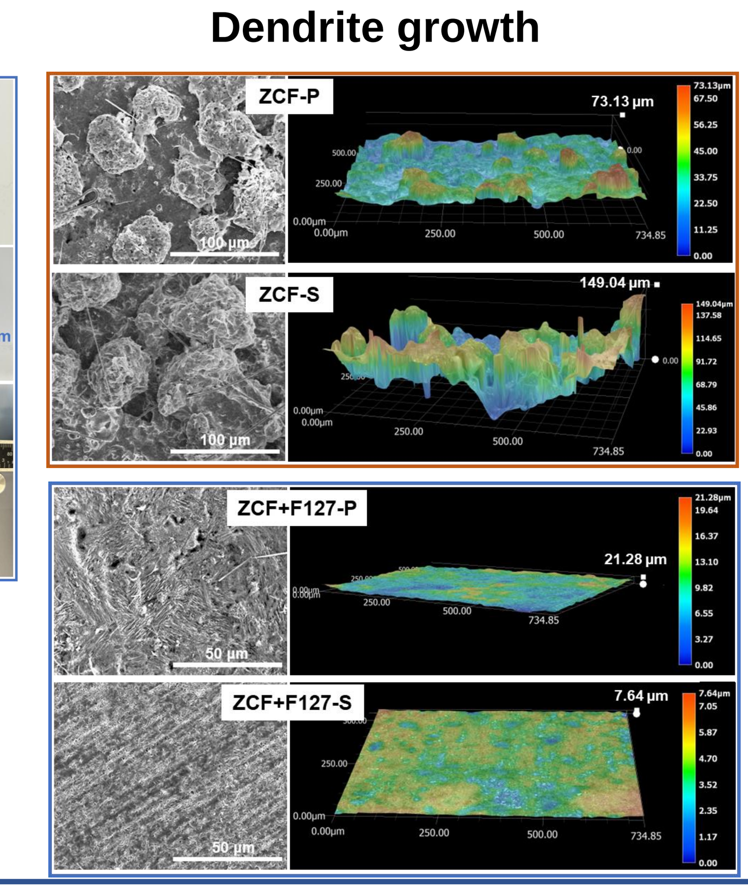
Soaking experiment



Volume expansion



Dendrite growth



- Alleviate corrosion, HER
- Suppress surface passivation
- Inhibit dendrite growth

Conclusions

- Amphiphilic Pluronic triblock copolymers are proposed as a new class of electrolyte additives to stabilize the Zn metal/electrolyte interface.
- Pluronic additives create a hydrodynamic layer between Zn and electrolyte, regulating the interface chemistry by forming localized hydrophobic confinement and modulating smooth Zn^{2+} distribution.
- The effectiveness of Pluronic additives depends on their EO/PO composition, block length, molecular weight, and structure.

Future work

- Investigating how key parameters of Pluronic (e.g., EO/PO composition, EO block percentage, and molecular weight) affect the Zn anode/electrolyte interface.
- Studying the impact of normal and reverse Pluronic structures on Zn anode stabilization.

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Reference:

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