

Final report to Åforsk foundation

Project: 21-130

Title: **Dendrite- Corrosion- and Thick Anode-Free Zn ion battery**

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## **Abstract**

The project's objective is to develop a Zn battery free from dendrites, corrosion, and anodes, utilizing a water-in-salt electrolyte (WiSE) with a focus on  $\text{Zn}^{2+}$  ion-conducting polymer electrolytes. Successfully reaching its goal, the project has demonstrated a long-lasting, dendrite, and corrosion-free Zn battery using WiSE. Also, it demonstrated an anode-less Zn-lignin battery. The innovative use of polymer-based WiSE, designed to suppress hydrogen and oxygen evolution reactions, has paved the way for depositing Zn and showcasing dendrite-free Zn-based devices, including batteries and supercapacitors. The project has achieved the efficient ionic transport of  $\text{Zn}^{2+}$  in highly concentrated polymer electrolytes. This innovative study is the first of its kind employing aqueous polymer electrolytes for dendrite and corrosion-free Zn plating, overcoming persistent challenges associated with conventional aqueous electrolytes. The project has yielded numerous promising research outcomes, resulting in the publication of five papers (*Advanced Materials*, *Chemistry of Materials*, *Journal of Materials Chemistry A*, *Advanced Sustainable Systems*, etc.) and two unpublished papers. We believe that this project will not only advance fundamental research in electrolytes and Zn batteries but also significantly foster the practical application and development of Zn batteries. This was achieved by the successful implementation of the three work packages as below:

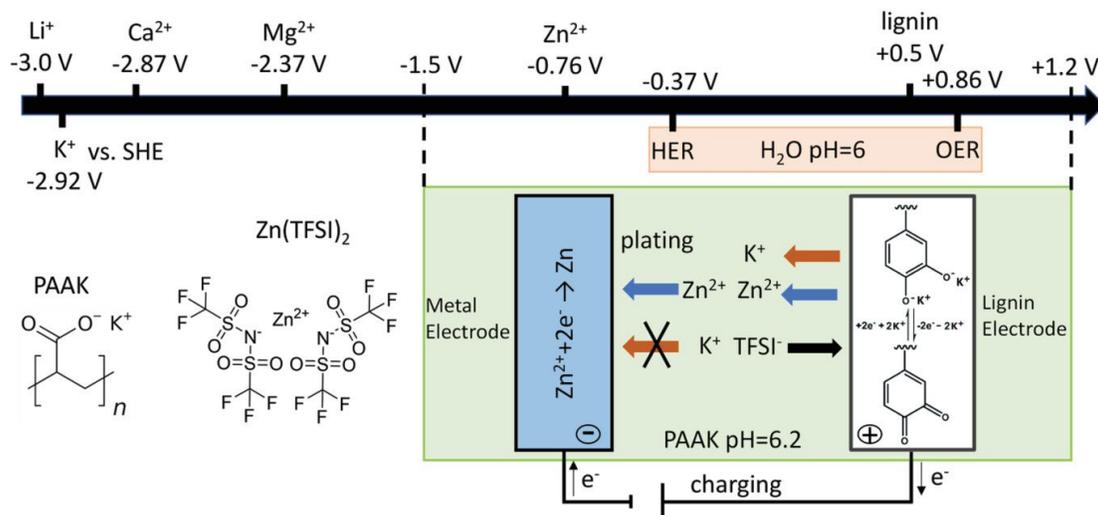
- WP1: Design and selection of electrolyte
- WP2: Electrodeposition of Zn on different substrate
- WP3: Cell fabrication using WiSE

The obtained results and related publications are discussed in the following parts based on all work packages.

### WP1. Design and ionic transport properties of water-in-polymer salt electrolyte

**Related Publications:** *Adv. Sustain. Syst.*, **2023**, 7, 2200433; *Chem. Mater.*, **2023**, 35, 6382.

Aqueous electrolytes are an attractive class of electrolyte primarily due to their high ionic conductivity, low cost, nonflammability, and environmentally benign nature. However, they are limited by a narrow potential range of operation (1.2 V). The project started with the development of polymer based WiSE where potential range for operation can be extended beyond 1.2 V. Potassium polyacrylate (PAAK) was chosen as WiSE because polyacrylates are non-flammable, non-toxic, non-fluorinated, cost-effective and possess flexible polymer chain. The highly soluble nature of polyacrylates makes them a suitable choice for WiSE electrolytes as a substantial quantity of salt can dissolve in a minimal amount of water. The measured electrochemical stability window (ESW) of PAAK was found to be 3 V.

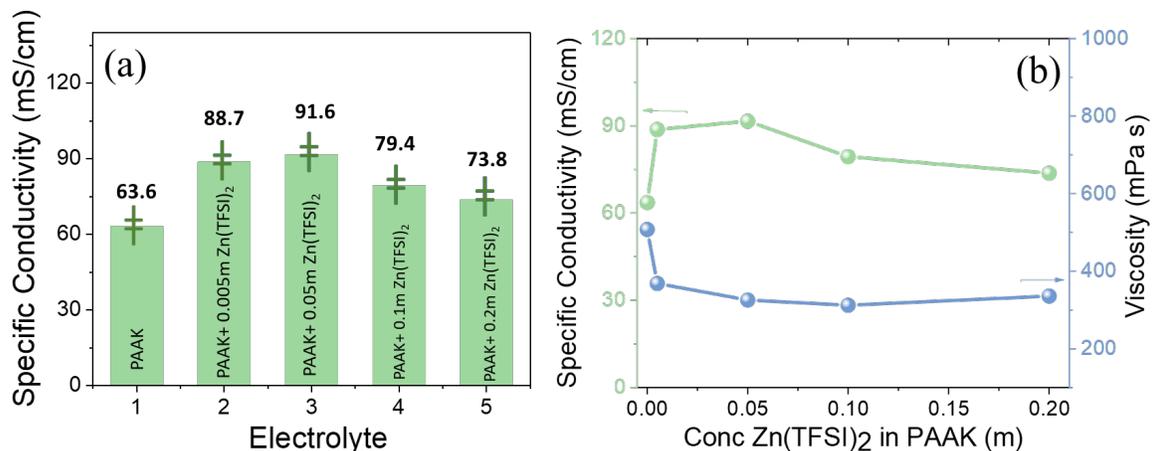


**Figure 1:** Redox potentials of various metal cations and ESW of PAAK showing that  $\text{Zn}^{2+} \rightarrow \text{Zn}$  redox potential lies well in the ESW of PAAK which suggests that Zn can be plated and stripped using PAAK. Chemical structures of the relevant redox systems and polymer salt are shown.

Inspired by literature work suggesting that Zn can be electroplated using WiSE due to low hydrogen evolution rates (a major drawback of Zn metal with aqueous electrolyte) our aim is to

use PAAK as a background aqueous electrolyte for Zn batteries where WiSE can be prepared by adding Zn salt in PAAK. The electrodeposition potential of  $Zn^{2+}$  ( $-0.76$  V versus standard hydrogen electrode [SHE]) occurs at a more positive potential than electrodeposition of  $K^+$  ( $-2.9$  V versus SHE) thanks to the electrochemical stability window of PAAK (Figure 1).

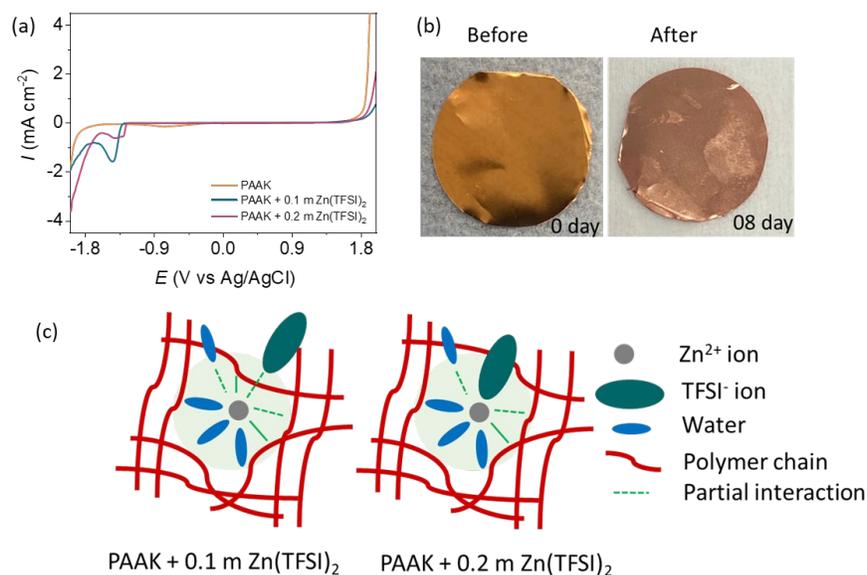
Various quantities of zinc bis(trifluoromethanesulfonyl) imide [ $Zn(TFSI)_2$ ] ranging from 0.005 to 0.2 m, were incorporated into PAAK to formulate a WiSE. Beyond this concentration, Zn salt was no longer soluble in PAAK. The ionic conductivity and viscosity of all WiSEs were measured. The findings revealed that the ionic conductivity exhibited an increase with the rising concentration of  $Zn(TFSI)_2$  salt, reaching 63.6 mS/cm for 0.005 m, and further increasing to 88.7 mS/cm and 91.6 mS/cm for concentrations of 0.05 m in PAAK. However, a subsequent addition of  $Zn(TFSI)_2$  resulted in a decrease in ionic conductivity, dropping from 91.6 mS/cm to 73.8 mS/cm (Figure 2a). Additional characterization involved studying the rheology of PAAK with varying concentrations of added  $Zn(TFSI)_2$  salt. The viscosity of pure PAAK measured at 530 mPas, while the introduction of  $Zn(TFSI)_2$  salt led to a reduction in viscosity (312 mPas for 0.1 m  $Zn(TFSI)_2$  and 336 mPas for 0.2 m  $Zn(TFSI)_2$ , respectively, as depicted in Figure 2b).



**Figure 2:** (a) Ionic conductivity and (b) viscosity of various PAAK and  $Zn(TFSI)_2$  based electrolytes.

### Estimation of ESW of prepared electrolytes and ionic transport mechanism study in PAAK and PAAK based hybrid electrolytes

ESW of prepared hybrid electrolyte is determined using a three-electrode setup, consisting of a glassy carbon working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode by linear scan voltammetry method. The linear scan voltammetry graph showed an exponential increase in current which could be associated with HER and Zn deposition peak in PAAK-Zn(TFSI)<sub>2</sub> at -1.4 V vs Ag/AgCl suggests a possible mechanism for the reduction of Zn<sup>2+</sup> → Zn(s), which is required for Zn-based batteries. Further, no significant corrosion was observed on the surface of Cu when dipped in WiSE for more than a week (Figure 3b). Lastly, Raman spectroscopy was also performed to study the interaction between different ionic species. Raman spectroscopy results indicate strong interaction between TFSI<sup>-</sup> and its surrounding in the PAAK-based electrolytes.



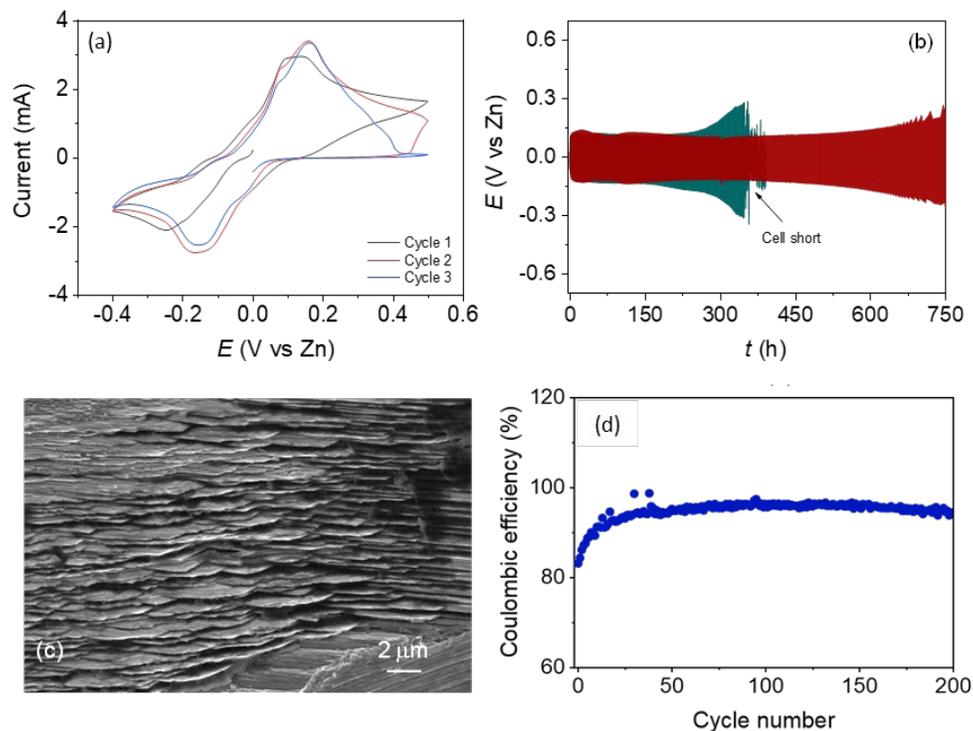
**Figure 3:** (a) Linear scan voltammetry of WiSE which showed no redox activity in PAAK electrolyte at -1.4 V vs Ag/AgCl however, there is redox peak at this potential when Zn salt being added. (b) Digital image of Cu foil before and after dipping in PAAK + Zn(TFSI)<sub>2</sub> hybrid solution (c) illustrates the solvation structure of prepared WiSE.

Theoretical and experimental results suggest that ionic transport in PAAK occurred via transport of hydrated cations (*Chem. Mater.*, 2023). We further went on to understand the ionic transport properties of PAAK-Zn(TFSI)<sub>2</sub> system using simulation method. The solvation structure of PAAK was changed when Zn(TFSI)<sub>2</sub> was added. Typically, in conventional electrolyte Zn<sup>2+</sup> ions are coordinated with six water molecules and there is a lot of free water around the solvation

sphere of Zn. However, in our case we found that Zn was solvated by 3.2-3.3 water molecules which suggests the scarcity of water molecules for perfect solvation. To compensate for the charges on  $\text{Zn}^{2+}$  ion  $\text{PAA}^-$  and  $\text{TFSI}^-$  anions are also involved in solvation of  $\text{Zn}^{2+}$  ions (Figure 3c).

## WP2: Electrodeposition of Zn on different substrate

Next, the electrodeposition of Zn was studied on Zn, Cu and Ti substrate in  $\text{Zn}||\text{Zn}$ ,  $\text{Cu}||\text{Zn}$  and  $\text{Ti}||\text{Zn}$  half-cells. It was found that Zn can be electroplated on these substrates though the rate capability of deposition was limited primarily due to the low concentration of Zn salt in PAAK. Zn can be electroplated on Zn up to 750 h without cell failure (Figure 4b) with layer-by-layer deposition (Figure 4c). Further, we estimated the Coulombic efficiency (CE) and cyclic stability of Zn deposition on Cu and Ti substrate. Though Zn can be deposited on both substrates, the CE and cyclic stability for Zn deposition on Ti was found superior to Cu substrate. > 95% of CE was observed for Zn deposition on Ti substrate up to 200 cycles (Figure 4d) whereas, 90% of Coulombic efficiency up to 12 cycles was observed for  $\text{Cu}||\text{Zn}$  cell.



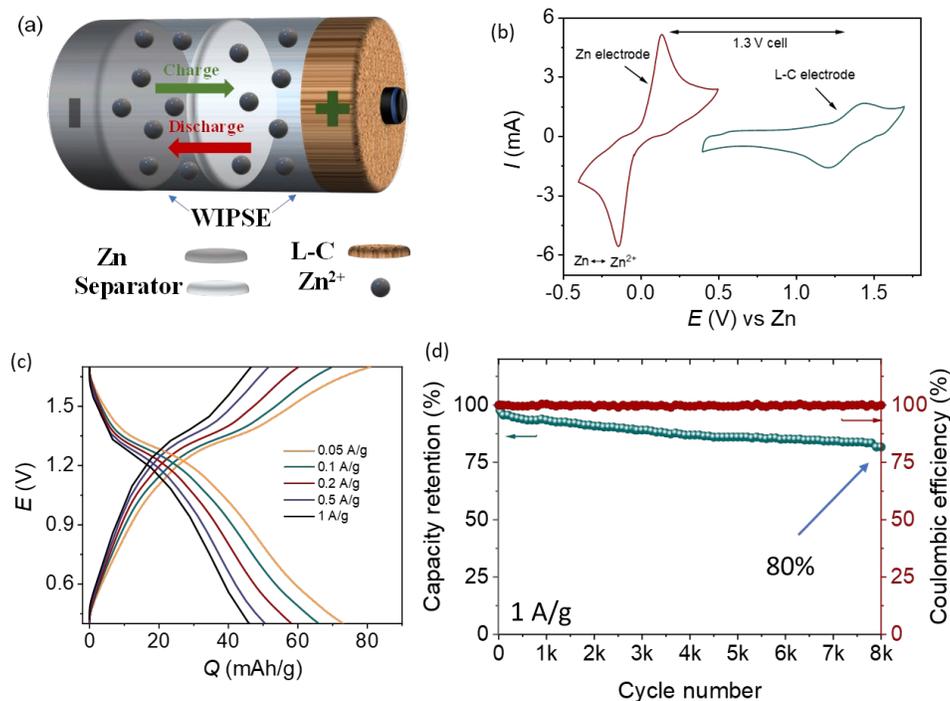
**Figure 4:** (a) CV of the cell built using deposited Zn on Cu as working electrode and Zn as counter electrode. (b) long time galvanostatic charge-discharge (GCD) profile associated with Zn plating/stripping on Zn. (c) SEM images of Zn electrodes after 750 cycles in PAAK+ 0.2 m

Zn(TFSI)<sub>2</sub> (d) CE related with Zn deposition on Ti in a Ti||Zn based symmetric cell in PAAK+ 0.2 m Zn(TFSI)<sub>2</sub> to observe reversibility of Zn deposition.

### WP3: Cell fabrication using WiSE

#### Zn-lignin battery (Figure 5)

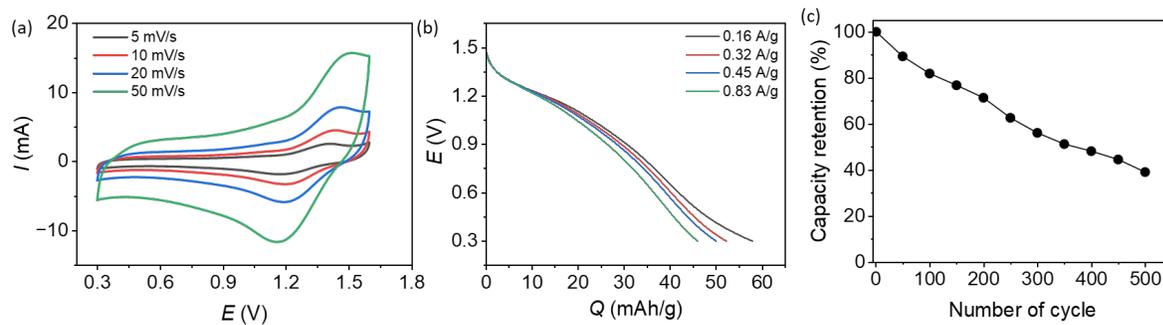
After plating/stripping investigation, we first fabricated Zn-lignin battery where Zn was used as anode and lignin/carbon composite was used as cathode. The idea here was to use pristine lignin without carbonizing it and therefore, it needs to be combined with conductive agent to make it electronically conductive which leads us to lignin with carbon as a cost-effective material. The Zn-lignin battery in PAAK + 0.2 m Zn(TFSI)<sub>2</sub> as WiSE displayed 80 mAh/g of specific capacity, 23 Wh/kg of maximum specific energy, >80% retention in specific capacity and < 99% CE up to 8000 cycles. This is one of best performance in terms of cyclic stability of Zn batteries was achieved.



**Figure 5:** (a) Schematic illustration of Zn-lignin battery in WiSE (b) CV of Zn and lignin/carbon electrodes in half-cell shows their electroactivity in different potential range. (c) galvanostatic charge-discharge profile of Zn-lignin battery (d) cyclic stability shows capacity retention of battery up to 8000 cycles at 1 A/g current rate.

### Anode-free Zn-lignin battery (Figure 6)

Finally, we fabricated Cu||lignin/carbon as anode-free battery using WiSE which reduces the thickness and weight of device. The performance was studied using CV and galvanostatic charge-discharge (GCD). The device in CV showed a pair of redox peaks originated from the redox activity of lignin. Also, the device showed achievement of maximum 60 mAh/g of specific capacity and ~40% retention in specific capacity up to 500 cycles. The cyclic stability obtained here is not as good as the case for Zn||lignin/carbon battery which could be attributed to the poor coulombic efficiency of Zn deposition on Cu using this electrolyte which demands more in depth understanding of system.



**Figure 6:** (a) CV and (b) galvanostatic charge-discharge profile of Cu|| lignin/carbon battery (c) cyclic stability shows capacity retention of battery up to 500 cycles at 0.83 A/g current rate.

### Summary

To summarize, Zn-lignin battery was demonstrated which showed outstanding cyclic stability without any dendritic growth and corrosion. Further, we also validated anode-free Zn-lignin battery. The project provided a new strategy to deal and overcome the long-standing problem of dendrite growth and underutilization of Zn electrode which will certainly help to design and develop new polymer electrolytes with suppressed parasitic processes. These promising results have inspired new research in this field. Our manuscript on Zn-lignin is submitted and few have been already published using the support of Åforsk foundation.

### Project implementation

Project was started on time and principal investigator worked on the project with part time help from PhD student Divyaratan Kumar. Overall, the project was executed as per the plan, and all work packages were successfully demonstrated.

**Research articles support by this project**

1. D. Kumar and Z. Khan et al. “*Water-in-polymer salt electrolyte for long-life rechargeable aqueous Zinc-lignin battery*” Submitted.
2. Z. Khan et al., “*Sulfonated Cellulose Membrane for Zn ion Hybrid Capacitors*” Submitted.
3. Z. Khan et al., “*Mass Transport in “Water-in-Polymer Salt” Electrolytes*” *Chem. Mater.*, **2023**, 35, 6382.
4. A. Rahmanudin et al. “*Sustainable stretchable batteries for next-generation wearables*” *J. Mater. Chem. A*, **2023**, 11, 22718.
5. Z. Khan et al., “*Does Water-in-salt Electrolyte Subdue Issues of Zn Batteries?*” *Adv. Mater.*, **2023**, 35, 2300369.
6. S. A. Patil et al., “*2D Zinc Oxide – Synthesis, Methodologies, Reaction Mechanism, and Applications*” *Small*, **2023**, 19, 2206063.
7. D. Kumar et al., “*Zinc salt in “Water-in-Polymer Salt Electrolyte” for Zinc-Lignin Batteries: Electroactivity of the Lignin Cathode*” *Adv. Sustain. Syst.*, **2022**, 7, 2200433.